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THE

PHYSICAL REVIEW.

THE TRANSMISSION OF THE IONIZED EXHALATIONS OF PHOSPHORUS THROUGH AIR AND OTHER MEDIA.[1]

By C. Barus.

I. The experiments of the present paper have been made by an electrical method. They relate to the decay of the ionization of phosphoric dust in the lapse of time, and to the transmission of the same through layers of air, or other media, or barriers. I hope to decide whether a form of radiation is presumable, or whether the case is merely that of an ionized gas exhaled by slowly oxidizing phosphorus. The results which I have obtained are remarkably similar to the behavior of thorium recently investigated by Rutherford,[2] and the theory of the phenomenon might be given in accordance with the better established principles as he has done. I shall venture, however, to treat the case in a simple and direct manner, in order to present it more consistently with my last paper[3] on the same subject, in which the attempt was made to arrive at the ion velocity of phosphoric dust by a non-electrical method.

[1] Communicated with the permission of the Secretary of the Smithsonian Institute.

[2] Phil. Mag. (5), XLIX., p. 1, Jan., 1900.

[3] Science, XI., p. 201, Feb. 9, 1900. The ionization of phosphoric dust was known to Matteuci, and has been studied since by Neccarri and by Bidwell. I believe to have been the first to point out its remarkable activity in producing condensation, and the substance is specially interesting to me because of this property. Cf. Bull., No. 12, U. S. Weather Bureau, 1895.

Let k be the ion velocity of the phosphoric dust particle, normally to a charged wall, A. The prism of phosphoric air which reaches A in one second will, for any appreciable length in the direction of k, be at an average potential zero, and its successive layers will on the average show no charge, although saturated with the ionized agency stated. Considered non-statistically, however, the individual sections at molecular distances apart must convey immensely different charges successively, the distribution of charge or of potential on successive sections following a law something like Maxwell's, for instance, relative to the distribution of velocity among molecules in the kinetic theory of gases. To deal with the problem in this broad form would make it needlessly cumbersome, without conducing to the present purposes. Apart from this, it seems possible to obviate the question of distribution somewhat as follows:

Suppose the distribution of potential in the direction of k is enormously variable as compared with the potential of A, in such a way as to give preference neither to positive nor to negative values. A will lose charge if its potential is instantaneously greater than that of the section which meets it; it will receive charge in the opposite case. A at potential zero, therefore, neither receives nor loses charge, since the number of sections reaching A in an appreciable time carry equal and opposite charges in like distribution. If the charge on A is positive there must then be fewer layers which impart charge to A and more layers which withdraw it than in the preceding case, since the average charge on the layers is still zero. Hence A will be discharged in the lapse of time and this more rapidly as its potential is higher. Precisely the reverse will happen if A is negatively charged. Hence to avoid the law of distribution specified I suppose that the charge per square centimeter on A is relatively so small that if it is increased n times, there will be n times fewer layers to charge it and n times more layers

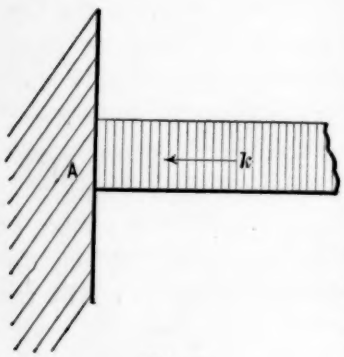

Fig. 1.

to discharge it than in the initial case. In other words I regard the charge on A per square centimeter small enough to correspond to a linear element of the law of distribution of charges along the length of the prism k. Thus the rate of A is caet. par. proportional to Q, its excess above the average charge of the advancing ionized sections which merge into A.

If n be the total number of ions per cubic centimeter, and ϵ is proportional to the charge (positive or negative) carried by each, $k\ n\cdot\epsilon$. is the total quantity of free electricity of both kinds promiscuously carried to A, per second per square centimeter. The rate of discharge of A is thus $-dQ/dt = Q\cdot n\cdot k\cdot\epsilon$, where the constant of proportionality is contained in ϵ. The integral of the equation is $Q = Q_0\varepsilon^{-knet}$ and the potential of the charged plate therefore

$$\varphi = \varphi_0\varepsilon^{-knet} \qquad (1)$$

in the lapse of time, t, after charging to the initial potential φ_0.

If instead of the plate A, a cylindrical surface of rádius r be given like the core of a tubular condenser, for instance, the number of particles reaching the surface per square centimeter per second is $n(k + k^2/2r)\epsilon$. Thus $-dQ/dt = Q\cdot n(k + k^2/2r)\epsilon$, and

$$\varphi = \varphi_0\varepsilon^{-n(k+k-2r)\epsilon t}. \qquad (2)$$

If r is infinite equation (1) is reproduced.

Corresponding equations follow for the case of charging the electrometer; but as for practical reasons my work is confined to discharging condensers, further mention is superfluous here.

The conveyance of charge into the ionized region would be similarly explained, virtually in the usual way, following Clausius. Through any interface in the ionized region two such prisms may be imagined, traveling in opposite directions. They travel to and from a boundary. The motion of the prism k is an abstraction; but if I accentuate it here, I do so because in the present investigation with phosphorus it may run closely parallel to the actual state of things. When the phosphorus grid is placed on a smooth clean surface, the position of the discs is soon marked by apparent grease spots, due to deliquescing phosphoric oxide which has diffused across. Virtually therefore an outgoing current, originating in the

phosphoric source is continually kept up, whether electricity is demonstrably conveyed or not.

In the annexed table, I have given an example of the results, which is sufficient, inasmuch as the large number investigated present throughout the same character. The following figure shows the method of experiment.

B_2 is a water battery of 48 volts, permanently charging the quadrants of an Elliott electrometer, one of which is always earthed as controlled by the switch S_2. B_1 is a storage battery (20 cells suffice), one pole of which is kept earthed as determined by the switch S_1, to be closed momentarily in charging. The other terminal charges the two condensers in parallel, MN in the electrometer, and CP for the ionization experiment. The plates M and P are also permanently earthed. N communicates in the usual way, with the needle of the electrometer, which is thus at the same potential as the plate C. P is a phosphorus grid, consisting of two sheets of wire gauze facing each other and placed closely together so that between them thin discs of phosphorus may be secured. As the air has free access to P on all sides, the medium between C and P is heavily charged with phosphorus dust. The essential precautions to be observed in work of this kind will be given elsewhere. Barriers are placed for examination between C and P quite out of contact with the former plate.

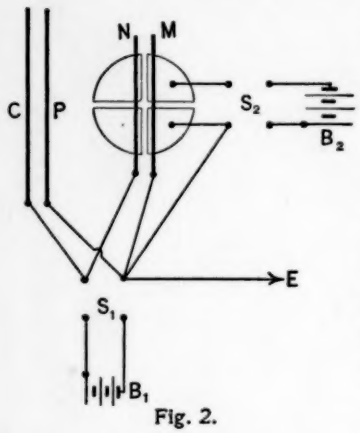

Fig. 2.

Table I. shows the leakage through the condenser CP when the plates are $d = 4$ centimeters apart, a relatively large distance. The exponential character of the law of discharge is manifest, but the decrease is throughout faster than can be reproduced by a simple geometric progression of the kind premised above. This might plausibly be ascribed to the waning activity of phosphorus itself in the lapse of time, and hence $c = n \cdot k \cdot e \cdot \log \varepsilon$ is necessarily a decreasing quantity as n, the number of particles per cubic centim. is sup-

TABLE I.

Permanence of phosphorus emanation.

Absorbent Medium.	Distance apart.	Time		Observed Potential Difference.	Computed Potential Difference.	$c = nke \cdot \log e$
		d	t			
Air.	4 cm.	10 h. 0 m.	0 m.	40.0 volts.		.0007
		10	10	39.0		
		15	15	39.0		
		20	20	38.6		
Air saturated with phosphoric dust.	4 cm.	10 h. 27 m.	0 m.	39 volts.	39 volts.	.0360
		28	1	35	36	
		29	2	32	33	
		30	3	29	31	
		31	4	27	28	
		32	5	25	26	
		33	6	23	24	
		34	7	21	22	
		35	8	20	20	
		36	9	19	19	
		37	10	17	17	
		38	11	16	16	
		39	12	16	15	
		40	13	15	13	
		46	19	13	—	
		51	24	13	—	
		57	30	9	—	

plied at a diminishing rate by the phosphoric source. Direct experiments negatived this supposition except for small distances, as the following examples chosen at random from many results of the same kind demonstrate.

TABLE II.

Decay of the ionizing activity of phosphorus.

Time	2h. 44m.	2h. 44.5m.	2h. 45m.	2h. 45.5m.	$d = 3$ cm.
Potential difference	35.6	32.4	29.4	26.8 (volts)	
Time	5h. 22m.	5h. 22.5m.	5h. 23m.	5h. 23.5m.	$d = 3$ cm.
Potential difference	35.4	32.4	29.4	27.0 (volts)	

According to the above table the rate of discharge of the freshly charged condenser before and after an interval of nearly 3 hours is not discernably different. The successive values of c were

Time	2h. 45m.	2h. 56m.	3h. 17m.	3h. 48m.	4h. 18m.	4h. 46m.	5h. 23m.
$c =$	.081	.078	.086	.078	.078	.070	.080

Fluctuation of temperature and air currents account for these irregularities. With plates 1 centim. apart the values of c were

Time	10h. 20m.	26m.	37m.	47m.	60m.	11h. 28m.	(12h. 1m.)
$c=$	.39	.39	.37	.34	.35	.34	(.33)

The last datum was obtained on readjusting the plates. Fluctuations here are greater, amounting to .05/68 or .0007 per minute, while the value .0009 is found in connection with other experiments below.

Thus it is improbable that in 15 minutes or less (usually less than 5 minutes), which outlasts the time of a single series of observations there should be any appreciable diminution of the ionizing potency of the phosphoric source. As I have not made up my mind on a satisfactory explanation I give below an exhibit of the inadequacy of the simple geometric equation. Let the observations be separated into two halves, and the constant c be computed from corresponding members, φ, t, and φ', t', of the two series. The values c and t of the table show the datum so obtained, and the mean time for which it holds. If the process is repeated to get the ratio of increments δc and δt of the values just found, the data $\delta c/\delta t$ of the table follow. These ratios are practically constant in the same series, but differ widely in different series, *i. e.*, with c. Let the mean c corresponding to each ratio be found as in the table. Then if $\delta c/\delta t$ be computed a datum is obtained, which though fully independent of c, is restricted to narrow limits. Thus in place of the above equation there follows a double exponential law

$$\varphi = \varphi_0 \varepsilon^{-\varkappa_\varepsilon - \gamma t' \varepsilon t}$$

expressing that some independent action has for the time t' been decreasing the number of particles at the rate γ. If C corresponds to c as N corresponds to n, $C/c = 10^{\gamma t' \log \varepsilon}$. The last column shows the values of C found in this way. Compared with c they are constant enough to plausibly suggest the action of some independent cause of decay, such as one would naturally attribute to the source. As this is untenable, one may note that the existence of a countercurrent, or the occurrence of a species of polarization is not unreasonably suggested.

Table showing the insufficiency of a simple geometric progression. Plates 4 centim. apart.

$t=\frac{t_1+t_2}{2}$	c	$\delta c/\delta t$	Mean c.	Mean t.	$\gamma=(\delta c/\delta t)/c$	C
4	.0374	.0023	.0327	10 h. 31 m.	.071	.0374
5	348	18	312	32	59	376
6	331	24	254	34	93	387
7	309	20	222	36	93	393
8	280					384
9	275					406
12	177					346
15	136					340
10	.0076	.0005	.0059	11 h. 51m.	.085	.0076
13	55	3	45	54	60	73
17	42					73
21	35					87

2. I next investigated the change of n, the number of particles per cubic centimeter with the distance between the condenser plates. The farther away the ions move normally from the phosphorus grid, the fewer will have survived. As at first trial I will suppose that the same relative number of ions decays per second in each layer. Thus $-dn/dx = an$ whence $n = n_0\varepsilon^{-ax}$. If $c = n \cdot k \cdot e \cdot \log \varepsilon$ as given above, $c/c_0 = n/n_0$. The following table is a summary of a completed series of experiments computed in this way. Since for

TABLE III.

Transmission of phosphoric dust in air. Summary: $c = nke \log \varepsilon$ $c/c_0 = n/n_0$ $n = n_0 10^{-ax}$ $a = .25$.

x	Mean time.	Corrected.[1]		Corrected c observed.	Corrected c computed.	10^{-ax}
		c	c'			
1.7 cm.	11 h. 18 m.	.200	.200	.200	.200	.376
5.7	22	.023	.196	.024	.020	.038
2.5	32	.120	.187	.128	.126	.237
11.5	43	.002	.178	.002	.001	.001
1.8	12 h. 3	.130	.160	.162	.188	.355
3.7	14	.033	.150	.044	.064	.119
1.7	25	.140	.140	.200	.200	.376

[1] The time correction is here made linearly. At $x = 1.7$, the value of c fell from .20 to .14 in 67 minutes, *i. e.*, .0009 per minute. This result is referred to above in relation to Table II.

any two values of x, c/c' is a constant, the observed value c is to be referred to a fixed value c' ($x = 1.7$ centimeter) corrected for the apparent decreased intensity of phosphoric ionization above referred to. These values c' are given in the table as well as the values c reduced in terms of them.

The table deduces the mean value of a to be .25, whence it follows that at $1/a = 4$ centimeters, the number of ions which still survive is but 1/10 of the original number. Similar ratios $n/n_0 = 10^{-ax}$ are given in the last column. For $x = 1$ cm., 5 cm., .1 cm., the relative numbers are $n/n_0 = .56, .75, .94$ showing how rapidly saturation is reduced even close to the phosphorus grid.

The above table exhibits the general character of the phenomena fairly well. It is, however, theoretically more probable (following the suggestion originally given by Laplace in his theory of capillarity, and recently by Van der Waals in the kinetic theory of gases) to suppose the rate of decay to vary as the square of the number of ions per cubic centimeter. In other words, $-dn/dt = \beta' n^2$ or since $c = kne \log \varepsilon$, $1/c - 1/c_0 = \beta' x/ke \log \varepsilon$. Hence $c = c_0/(1 - \beta x)$, where $\beta = \beta' c_0/ke \log \varepsilon$.

I have given the constants so obtained in the following table:

TABLE IV.

Summary: $c = c_0/(1 + \beta x)$; $c/c_0 = n/n_0$; $c_0 = -.100$; $\beta = -.88$.

x	c	Corrected c observed.	Corrected c computed.
1.7	.200	.200	.200
1.8	.130	.162	.172
2.5	.120	.128	.083
3.7	.033	.044	.044
5.7	.023	.024	.025
11.5	.002	.002	.011

Hence the equation $1/c - 1/c_0 = \beta x/c_0$ where $\beta/c_0 = 8.8$ is closely in accord with the observations, but the result for small values of c is absurd, since c_0 is negative. Inasmuch as the errors in the last two tables are cumulative, better results than this were not to be expected, seeing that a reason for the apparent decay specified has not been made out. Taking the observations at their face value preference must be given to the exponential first discussed. Neither

of these expressions, however, can be expected to represent the case fully, for in both differential equations all allowance for those particles which escape laterally from between the plates, is left out. The term ignored may be much more than a correction; but it would be premature to approach the question in this form before the phenomenon as a whole is better understood. Moreover, experiments with a small phosphorus grid at potential zero facing a relatively large charged plate, would offer a disposition better adapted to facilitate computation. Here the lateral loss may be made negligible.

3. The endeavor is finally to be made to decide whether the ionized particles exhaled by phosphorus are accompanied by some form of obscure radiation, or whether the reaction is restricted to an oxidation, the products of which escape at first in virtually a gaseous form. This is best done by placing barriers of thin material between the plates of the condenser, care being taken to prevent the phosphoric dust from passing around the barrier, yet allowing sufficient space for the access of air. It was my plan to fold the sheets box-like around the phosphorus grid kept at potential zero, so that escape around the edge would require a passage of 8–10 centims. to reach the other plate. This suffices, and the

TABLE V.

Transmission of phosphorus ions through barriers.

Barrier.	Thickness.	ϵ	Date.
Tissue paper.	.006 cm.	.092	Feb. 3.
" "	"	.018	" 4, A. M.
" "	"	.007	" 4, P. M.
Writing paper.	.010 cm.	.072	Feb. 3.
" "	"	.002	" 4, A. M.
" "	"	.002	" 4, P. M.
Filter paper.	.020 cm.	.011	Feb 4, A. M.
" "	"	.008	" 4, P. M.
Aluminum foil.	.003 cm.	.003	Feb. 4, A. M.
" "	"	.002	" 4, P. M.
Insulation.		.002	
None.		.500	

plates may then be placed quite closely together on opposite sides of the barrier. Energetic action is secured at a distance apart of about 1 centim.

Porous papers, like tissue or filter paper, transmit the emanation in small quantity, depending on circumstances not easily made out. Usually not more than a few per cent. of the emanation will pass even under favorable conditions. The large values found for writing and tissue paper on the first day, were not again obtained[1] in many subsequent experiments. They may be errors, though careful inspection of the results has revealed none. It is also possible that the emanation from phosphorus may be different under qualitatively different circumstances, apart from intensity.

The general result obtained is thus definitely against any obscure radiation. The emanation passes in quasi-gaseous form with great difficulty and loss even through very thin porous barriers. It is stopped by impervious media however thin. Oiled tissue paper cuts off the ions unconditionally. Permeability seems to decrease in the lapse of time, apparently as if deliquescing phosphoric acid clogged the pores.

4. In conclusion I will briefly advert to experiments made to detect ionization in other dust producers. The method selected consisted simply in blowing dust-laden air between the plates of the condensers, the current entering at the center of the earthed plate and escaping at the edges. Thus 86,000 cubic centims. of air bubbled through concentrated sulphuric acid in about 6 minutes produced an electric leakage equivalent to but $c = .0005$; while the leakage of the condenser before the experiment was $c = .0010$. Hence the effect was increased insulation to the exclusion of all traces of ionization. The same air current tested in the color tube gave an intensely opaque field, showing its condensation producing potency to be of high order.

Ammonic polysulphide tested in like manner gave similarly negative results. About 80,000 cubic centims. passed in 5 minutes through the condenser showed no leakage whatever, whereas, the

[1] The large values for tissue paper and larger values for filter paper ($c = .05$ to $.06$) have since been obtained under trustworthy conditions. Possibly the emanation from phosphorus may not be homogeneous in relation to temperature.

insulation leakage was originally equivalent to $c = .0006$. In this case, however, the air current produced only just perceptible darkening in the field of the color tubes, evidencing therefore but slight condensation producing tendency. The effect of this reagent on the color tube is in general very fleeting. When evaporating from the stopper of the bottle it is intensely active but only momentarily, as a rule. If however the current of air is replaced by a current of coal gas (which is itself somewhat dust-laden, as appears when the test is made with the color tube), the effect is much more persistent. Indeed the air of a large room if rendered impure in this way, reacts on the color tube for a longer interval than under any other easily producible conditions which I have found. The fleeting nuclei from ammonium sulphide seem therefore much more stable when preserved out of contact with an oxidizing medium like air, and the same is true for sulphuric acid in a measure, and for sulphur itself.

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AN HERMETICALLY SEALED TYPE OF CLARK STANDARD CELL.

BY H. T. BARNES.

OF the different types of Clark cell studied by the writer, a few hermetically sealed cells were made and briefly mentioned in another place.[1] The best of these cells, of the form known as the "sealed" cell, will be described somewhat in detail in the present paper. The advantage of a cell that can be completely closed by glass fusion is obvious. At the same time the cell should be moderately easy to construct, should embody strength and compactness, and should be perfectly portable. The present cell is primarily designed after the modified English Board of Trade model known as the B. O. T. "crystal" cell. It avoids the use of an amalgam button for negative electrode, which almost invariably ends by splitting the cell at the point where the negative terminal is fused through the glass, by the creeping of the amalgam along the wire. It includes the advantage of the "crystal" cell, *i. e.*, absence of diffusion lag, and has the extra advantage of being smaller and more sensitive. An important fact also is that the bulb of the cell containing the sensitive parts may be completely immersed in a water bath, or other form of thermostat, and at the same time is insulated thermally from the outside electrodes by the thick glass neck.

The arrangement of the cell will be best understood by reference to Fig. 1. In this the positive electrode is a platinum wire flattened at one end and amalgamated. The wire is enclosed in a glass capillary drawn from a small glass tube, shown in the figure, as the positive mercury cup. The negative electrode is a small zinc rod cast around a platinum wire and its enclosing glass capillary. This wire passes through the main fusion join *A*, and ends in the outer or negative mercury cup. As soon as the ingredients of the cell have been filled in through the open end, the final seal-

[1] H. L. Callendar and H. T. Barnes, Proc. Roy. Soc., 62, 117 (1897).

ing of the cell is made by quickly fusing the glass in the narrow neck, *B*. By placing a small quantity of mercury in the cups, terminals, pilot leads, or other connections can be inserted for comparison or test. When the cell is to be sent away or carried any distance, the mercury can be at once removed from the cups. The contents of the cell being in a firm mass, the cell may be kept in any position.

To construct the outer containing vessel, a glass tube, about one centimeter in diameter, is selected and cut about 15 or 16 centimeters long. This tube is drawn in the blowpipe flame at two places; one for the point of main fusion, *A*, Fig. 1, between 4 and 5 centimeters from one end, and the other *B*, so as to leave a bulb for the ingredients about 5 centimeters long. The restriction at *A* is to be left large enough to allow the zinc rod to pass through, while that at *B* should be large enough to allow of the insertion of the ingredients, through the remaining portion of the main tube not drawn down.

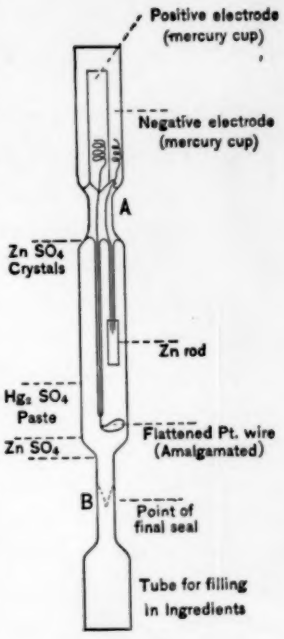

Fig. 1.

The positive electrode is made by drawing down a glass tube, of the same kind of glass as the main tube, 3 or 4 millimeters in diameter, into a firm strong capillary. This is shown at *P* in Fig. 2. The capillary should be long enough to reach from the main restriction, *A*, almost to the other restriction, *B*. A platinum wire, rolled flat for about a centimeter at one end, is passed through the capillary, and sufficient length left protruding into that portion of the tube not drawn down, which serves as the positive mercury cup. The capillary tube should be melted around the wire only at the end near the flattened portion. The amalgamation of the flattened end is done by heating red hot and cooling suddenly in pure mercury.

The negative electrode is made in the following way: a small mold of glass is constructed from a glass tube about 3 millimeters

in diameter and is filled with particles of absolutely pure zinc. These zinc particles are melted, and while melted, a platinum wire and a portion of its enclosing glass capillary is thrust in. On cooling and solidifying the glass mold is broken away, leaving the small zinc rod firmly attached to the capillary tube. This terminal is shown at *N*, Fig. 2. It should be long enough to reach from the seal *A* to the middle of the cell. Before inserting in the cell, the zinc rod should be scraped clean and bright and amalgamated by dipping into pure mercury upon the top of which a thin layer of dilute sulphuric acid is placed. By this means the zinc surface comes in contact with the mercury immediately after cleaning in the sulphuric acid, which is essential to ensure perfect amalgamation. After this process the rod should be most carefully washed free from every trace of acid and dried with filter paper.

Fig. 2.

In making the main fusion, the two electrodes are placed in position by inserting them through the restriction at *A*, the positive electrode held central by means of small wedges, and the glass melted uniformly until it runs together around the two wires in a firm thick neck. The join is then carefully annealed to avoid cracking in the glass, which is liable to occur around the point where the positive mercury cup is sealed in, or at the point where the negative wire passes through. Before placing the electrodes in the cell, the ends of the wires for the mercury cups may be amalgamated.

In filling the cell, it is turned upside down and a small quantity at a time of moist zinc sulphate crystals pushed through the narrow neck by means of a small stiff glass rod. Once through the neck they can be shaken down into place. Crystals are added until the zinc rod is well covered. The paste, consisting of the usual mixture of pure washed mercurous sulphate and zinc sulphate crystals, is then pushed through in the same way. The paste should completely cover the flattened platinum wire. A few zinc sulphate crystals are then pushed through until they form a thin layer over the paste. The neck is then cleaned and dried as much as possible with filter paper, and fused together quickly in a small blowpipe

flame. Very little heat is imparted to the glass beyond the neck, and what is passed to the ingredients is taken up by the thin layer of zinc sulphate crystals, thus avoiding any decomposition of the mercurous sulphate. The small bubble of air left after fusing the neck allows of the slight expansion of the materials and guards against the bursting of the cell. The completed cell, as in daily use in this laboratory, is shown by the photograph in Fig. 3, about two-thirds natural size.

Fig. 3.

PREPARATION OF THE INGREDIENTS.

Mercury.—For amalgamation the mercury should be, when very impure, twice distilled in vacuum. When moderately pure, a single distillation is sufficient.

Zinc Sulphate.—The ease with which the very purest anhydrouszinc sulphate is obtained from any of the standard chemical manu facturers, makes it quite unnecessary to treat the solution with zinc oxide for neutralization, as recommended by the older processes. In order to obtain the heptahydrate crystals, the anhydrous salt is dissolved in water and a solution saturated at 30° C. prepared. While at 30° a small quantity of pure washed mercurous sulphate may be added, but it is not always necessary. It would depend on whether there was a trace of zinc oxide in the anhydrous salt. It, however, will do no harm and is immediately removed by filtering the solution in a water-jacketed funnel at 30°. The clear filtrate is cooled in melting ice, and the supernatant liquid poured off from the batch of crystals produced. Should a yellow turbidity appear in the process of cooling, it shows that the solution containing the mercurous sulphate has been heated to 35° or over. It is better to avoid the yellow turbidity altogether by not heating above 30°, but if present, the crystals may be remelted and the solution filtered un-

til completely removed. The crystals produced in the melting ice are put aside in a stock bottle.

Mercurous Sulphate.—The purest mercurous sulphate should be obtained and washed by decantation several times, with pure distilled water. After the final washing the salt is caught on a filter and drained. When moderately dry it is transferred to a mortar and an equal quantity of zinc sulphate crystals added from the stock bottle. The mixture is ground into a thick paste with some pure metallic mercury and transferred to a second stock bottle, dark-colored or otherwise protected from the action of the light by black paper.

TESTS AND COMPARSIONS.

From a careful study of the change of E.M.F. with temperature, for the various types of cells devised, the following simple formula in millivolts was found to fit the observations most closely between 0°C. and 30°C.

$$E_t = E_{15} - 1.200\,(t - 15) - 0.0062\,(t - 15)^2 \cdots \qquad (A)$$

The analogous formula finally obtained by Kahle reads

$$E_t = E_{15} - 1.19\,(t - 15) - 0.007\,(t - 15)^2,$$

which is in remarkable agreement. By formula (A) the total change between 15 and 0°C. is 16.60 millivolts, while between 15° and 30°C it is 19.40 mv. At 30° the actual observed change diverges from this simple parabolic formula, increasing more rapidly as the temperature rises to 40°, when the sudden change of hydration of the zinc sulphate causes the E.M.F. to rise and follow a different curve. The character of the temperature curve above 30° and 40° has been studied by the author, and the details of the experiments have already been published.[1] In that place it was shown that formula A, when corrected by the additional term

$$-0.00006\,(t - 15)^3 \cdots \qquad (B)$$

holds with great accuracy over the range 15° to 40°C. Above 40° the following expression represents the hexahydrate branch of the curve

$$E_t = E_{39} - 1.000\,(t - 39) - 0.007\,(t - 39)^2 \cdots \qquad (C)$$

[1] H. T. Barnes, Journ. Phys. Chem., 4, 1 (1900).

It appears probable that the divergence from the simple parabolic formula (A) above 30° is due to some action of the mercurous sulphate at the higher points, which does not appear below 30°, and is also the cause, as has been pointed out, for the lower value given by the Clark cell for the temperature of inversion of the heptahydrate and hexahydrate (38°.78C.), as compared with the value given by solubility determinations, which places it more nearly at 40°C.

A sufficiently clear idea may be obtained of the accuracy and sensitiveness of the "sealed" cell by reference to the author's paper above referred to, on the inversion of the hepta- and hexahydrates of zinc sulphate in the Clark cell. However, various other data are available and hitherto unpublished on this form of cell, and may not be out of place here.

In Table I. are shown comparisons on several cells made at different times, with different materials. The differences in their E.M.F. are expressed in millivolts.

TABLE I.

Cell.	Jan. 1896.	Feb. 1896.	Feb. 1898.	May 1898.	Jan. 1899.
S_1	−0.11	−0.13	+0.07	+0.02	+0.00
S_3	−0.10	——	——	——	——
S_4	+0.05	+0.03	——	——	——
S_5	+0.10	+0.11	+0.13	+0.12	+0.17
S_6	+0.01	——	——	——	——
S_7	——	+0.01	——	——	——
S_{10}	——	——	−0.02	——	——
S_{11}	——	——	——	——	−0.05
nS_{11}	——	——	——	——	−0.05
S_{12}	——	——	——	+0.27	——
S_{13}	——	——	——	−0.05	——

The differences are of the order of $\frac{1}{10}$ of a millivolt; with the exception of S_{12}, which was tested rather too soon after being set up. Owing to its removal from the laboratory with S_{13} shortly after, no further tests were obtained. It is probable, however, that it may have contained a slight trace of acid from the amalgamation of the zinc, which could only be removed by very vigorous means, such as short-circuiting the cell, or otherwise by the lapse of time. In

fact, one of the best methods of aging a cell and bringing it into a steady normal condition is by short-circuiting it with a copper wire for half an hour or so after setting up. The reads in Table I. show the variation from the mean of cells S_1 to S_6. Comparisons of cells S_{10} to S_{13} were made indirectly to cells S_1 to S_6 by comparison with five B.O.T. test-tube "crystal" cells that have been in the laboratory since 1895. A comparison of the means of the five sealed cells with the five crystal cells showed that the former exceeded the latter by only 0.08 millivolt. The five crystal cells have maintained their relative differences in a very satisfactory manner, as will be shown in another place.

During the progress of the author's experiments on the specific heat of water in terms of the international electrical units, two of these sealed cells were used and frequent comparisons made for a little over a year. These comparisons are given in Table II., and

TABLE II.

$S_5 - S_1$			$S_5 - S_1$		
Date of Comparison.	Difference in mv.	Temp. of Comparison.	Date of Comparison.	Difference in mv.	Temp. of Comparison.
Nov. 16, 1897.	0.10	15°	Apr. 12, 1898.	0.08	15°
Feb. 4, 1898.	0.06	"	" 20, "	0.10	"
" 22, "	0.02	16°	May 4, "	0.12	"
Mar. 1, "	0.03	"	" 5, "	0.10	"
" 3, "	0.02	14°	" 9, "	0.13	"
" 5, "	0.06	15°	" 14, "	0.11	"
" 9, "	0.05	"	" 23, "	0.10	20°
" 10, "	0.07	"	" 28, "	0.15	15°
" 11, "	0.04	"	June 10, "	0.10	21°
" 14, "	0.07	"	" 13, "	0.19	18°
" 16, "	0.06	"	" 17, "	0.12	"
" 23, "	0.07	"	July 23, "	0.10	20°
" 25, "	0.07	"	Sept. 10, "	0.16	19°
" 31, "	0.09	"	Oct. 14, "	0.17	14°
Apr. 2, "	0.06	"	Dec. 14, "	0.03	15°

will serve to show the way in which these cells may be relied upon to maintain their relative differences.

The variation in the difference between the two cells is so regular and consistent, never exceeding in the extreme case much more than 1 in 10,000, that over extended periods the difference can be

relied upon to one or two parts in 100,000. By taking sufficient care in the temperature and electrical measurements, this is about the order of agreement of this type of cell.

In regard to the temperature change and sensitiveness, some tests made on cell S_4 are given in Table III.

TABLE III.

Time after changing temp. of cell.	Total change of temperature.	Difference in mv. observed.	Diff. in mv. calculated by formula A.
5 minutes	15 to 0°C.	+15.90	+16.60
10 "	"	+16.44	"
60 "	"	+16.62	"
10 "	15 to 30°C.	−19.37	−19.40
30 "	"	−19.50	"

On returning to 30° from 50° C., the same cell showed a difference from its value at 15° of −19.62 mv. It is probable that had the cell been left at 30° in the first test longer than half an hour it would have shown a slightly larger difference. The total change between 15° and 30° by formula (*B*) is −19.60 mv., which is much closer to the observed value.

Table IV. contains tests made on cells S_4, S_5 and S_7, between 15°.36 and 23°.83 C.

TABLE IV.

Cell.	Total change in mv. observed.	Formula A.
S_4	−10.62	−10.62
S_5	−10.69	"
S_7	−10.62	"

Cell S_5 changed slightly more than the others, but the mean of the three cells will be a little in excess of formula (*A*), as is generally the case at the higher points.

The effect of a short circuit on one of these cells was shown by connecting the terminals of cell S_4 with a short, thick wire and obtaining comparisons of its E.M.F. during recovery after the wire was removed. In two and a-half minutes after short-circuiting for seven minutes, the E.M.F. was within three-tenths of a millivolt of

its original value. In ten minutes it was within two-tenths, and it had completely recovered in thirty.

For an account of the thermostats, potentiometer and temperature measuring instruments used in these tests, reference should be made to the author's earlier papers (in loc. cit.), where also the method of carrying out the experiments is described.

MACDONALD PHYSICAL LABORATORY, MCGILL UNIVERSITY, Feb. 14, 1900.

CONCERNING THERMAL CONDUCTIVITY IN IRON.

By Edwin H. Hall.

HAVING had occasion of late to examine with some care the information given by Landoldt and Börnstein and by Winkelmann concerning the thermal conductivity, k, of wrought iron and the temperature coefficient, a, of k, I have discovered so many inaccuracies, especially in Winkelmann, and have been so much impressed by the inconclusiveness of the showing, that I have felt moved to write a somewhat critical résumé of the methods and results in this limited but much worked field of investigation. I am the more induced to undertake this labor by the fact that even the most recent books published in English follow the custom of quoting the results obtained by Forbes as if they were the only ones worthy of especial mention, in spite of the fact that these results, for the best known of his bars, were long since disproved and superseded by work done on the same bar in the same laboratory.

It is true that Holborn and Wien published[1] some years ago the results of a discussion somewhat similar to that which I propose, but they did not publish their discussion; and, moreover, I find that in a number of particulars, especially in regard to the value of a, my conclusions are different from theirs. Where so much experimental work has been done, there is room for more than one attempt to estimate the value and results of that work. It is my hope to reach conclusions which may help to direct and make profitable future investigations. The recent interesting paper[2] of Liebenow, *Zur Thermodynamik der Thermo-ketten*, may seem to bring near the possibility of determining the thermal conductivity of metals from a study of their electrical conductivity and thermo-electric properties. But, whatever may be the final outcome, one of the first effects of Liebenow's paper must be to stimulate renewed

[1] Zeitschr. Ver. Deutsch. Ingen., Vol. 40, 1896.
[2] Wied. Annalen, June, 1899.

interest in the results obtained from the methods heretofore used for the measurement of thermal conductivity.

Landoldt and Börnstein give [1]

	Temp.	k.	Observer.
Eisen,		.1638	Neumann.
"	über 0°	.1587	Berget.
"	0°	.1988	Angström.
"	0°	.1665	Lorenz.
Schmiedeeisen,	0°	.2070	Forbes.
"	39°	.1485	H. Weber.

and the following temperature coefficients, that is, values of the constant α in the formula $k = k_0(1 + \alpha t)$:

Eisen	— 0.0002282	Lorenz.
" gewöhnl, 0 bis 300°	— 0.000611	Mitchell.
" gekühlt, 0 bis 300°	+ 0.000706	"

Winkelmann [2] gives in his table, without the dates,

Metal.	Temp.	k.	Observer.	Date.
Eisen,	0°	0.1665	Lorenz,	1881
"	0°	0.1988	Angström,	1861–4
"	über 0°	0.1587	Berget,	1890
"	ca. 15°	0.1648	Neumann,	1862
"	ca. 15°	0.1133	Wiedemann u. Franz,	1853
"	0°	0.1509	Mitchell,	1887
"	0°	0.172	Stewart,	1893
Schmiedeeisen,	0°	0.2070	Forbes,	1862–5
"	39°	0.1485	H. F. Weber,	1880

The temperature coefficients given by Winkelmann are

— 0.000038 from the work of Lorenz,
— 0.000517 " " " " Angström,
— 0.0006838 " " " " Forbes.

I shall follow in general a chronological order in my discussion, departing from it whenever there seems to be good reason for so doing.

[1] Physikalische Chemische Tabellen.
[2] Handbuch der Physik., part 2 of vol. 2.

Wiedemann and Franz.

"Es wurden zwei Stangen I. und II. von 5 mm. Dicke untersucht." This is, I believe, the whole explicit description of the iron, although it can be inferred from the description of the apparatus that the length of the bars was about 50 cm.

They worked with a considerable number of metals, but obtained comparative results only. It therefore seems idle to attempt now to derive absolute values of k from their data.

They appear to have been the first to make a systematic comparison of thermal and electric conductivities, although Forbes had many years before pointed out the apparent connection between these two properties in metals. Wiedemann and Franz did not measure, even comparatively, the electric conductivity of the bars; but trusted to the values found by others for similar materials. The table given by Winkelmann, Vol. 2^2, p. 277, to show their results differs in several particulars from that given by Wiedemann and Franz, and it is so badly aligned that in some cases it is impossible to tell to which metal the numbers given apply.

It is to be observed that Landoldt and Börnstein give no absolute values on the authority of these early experimenters.

Forbes, Angström and Neumann, working each by his own peculiar method, obtained results which they published about the same time. The method of Forbes was simpler, in theory, than the others, and will be discussed first.

Forbes (and Mitchell).

No other experiments upon thermal conductivity are so familiar to English-speaking people as those of Forbes, and the method which he originated and used is so well known that description of its general features is unnecessary here; and yet it is time for us to recognize the fact that the numerical results obtained by Forbes have only an historical interest, and that, if their publication in physical tables of the present day is to perpetuate a belief in their numerical accuracy, it would be far better to exclude them altogether from such tables. This statement I shall undertake to verify by what follows.

Forbes used two wrought-iron bars of somewhat different sizes. The better known of the two, called *D*, he describes a "a beautiful bar, 1¼ inch square and fully eight feet long." He gives its specific gravity as 7.79. The other bar was 1 inch square. Reduced to the C. G. S. system, the values which he found for *k* from the two bars were

1¼ inch bar.	1 inch bar.	
0.207	0.1536	at 0° C.
0.1567	0.1293	" 100° "

The great difference between the values of *k* given by the two bars at the same temperature has been explained as probably due to a difference in the quality of the iron; but in view of the subsequent history of bar *D*, and the general average of values obtained for iron by other experimenters, this explanation seems inadmissible.

Each bar gave a large negative temperature coefficient for *k*. Tait, after Forbes, worked with bar *D* and applied corrections, which Forbes had not done, for change of specific heat with change of temperature. The result was to make the temperature coefficient almost or quite disappear. Then Mitchell worked with the same bar. In accordance with the advice of Tait he used sometimes the ordinary method of Forbes, heating one end of the bar while all the rest of its length was freely exposed to the air of the room, and sometimes combined the heating of one end with a cooling of the middle in order to get a steeper gradient of temperature in the cooler parts of the bar. This variation of method produced a marked change in the values found for *k*.

Forbes had expressed his results in terms of the foot, minute, and thermal capacity of a cubic foot of water. Mitchell departed from this tradition far enough to express his results in terms of the foot, minute, and thermal capacity of a cubic foot of the iron at some one temperature. It was therefore not necessary for him to determine the specific heat of the iron; but he did undertake to introduce into the values obtained for *k* at different temperatures correction for change of specific heat with temperature. It seems probable that he used a somewhat too large temperature coefficient in making this correction.

Certain thermometer corrections were applied by Mitchell, the

effect of which corrections was to lessen considerably the values of thermal conductivity found for high temperatures as compared with those found for low temperatures.

The numbers which follow and the words accompanying them I have copied from Mitchell's paper:

Temperature C.		0°	100°	200°	300°
Iron (Ordinary).	Not corrected for specific heat change.	.0127	.0115	.0103	.0091
	Corrected for specific heat change.	.0131	.0123	.0115	.0107
Iron (Cooled Bar.)	Not corrected for specific heat change.	.01154	.01162	.01170	.01178
	Corrected for specific heat change.	.0119	.01274	.01358	.01442

"Iron (Ordinary)" refers to the "ordinary" Forbes's method, heat applied to one end of the bar the rest of which is exposed to the air. This is the "Eisen gewöhnl" of Landoldt and Börnstein's table. "Iron (Cooled Bar)" refers to the varied method, in which the middle of the same bar was cooled by a stream of water while the end was heated. This is the "Eisen gekühlt" of the same table. The great difference between the results of these two very similar methods throws much doubt upon the accuracy of the results obtained from either or both, so far, at least, as relates to the temperature coefficient, which has a large positive value in one case and a still larger negative value in the other case.

The values given by Mitchell are to be turned into C. G. S. units by multiplying them by 15.48 $C\rho$, where C is the specific heat at some one temperature, probably the temperature of the air, and ρ is the density. Winkelmann gets the value 0.1509 at 0°, which he puts opposite the name of Mitchell, by multiplying 0.0119 ("Cooled Bar," 0°) by $C = 0.105$ and $\rho = 7.8$. This reduction is probably not very far wrong, though a somewhat higher value for C might well have been used, but in reducing the values given by

Mitchell for k at higher temperatures, as Winkelmann does on page 280, he multiplies each by the specific heat of iron for the higher temperature in question, 100°, 200°, etc. The values which he thus gets for these higher temperatures are therefore doubly "corrected" for change of specific heat, once by Mitchell and again by Winkelmann. Fortunately, Winkelmann does not put these values into his final table.

Landoldt and Börnstein give no value of k from Mitchell; but, as we have seen, they give two values of a, its temperature-coefficient from his work, not perceiving, we may suppose, that "Eisen gewöhnl," "Eisen gekühlt," and "Schmiedeeisen" (Forbes) are one and the same bar D, one of the national monuments of Scotland. The temperature-coefficients which they give are obtained correctly from the values of thermal conductivity "corrected for specific heat change," quoted above from Mitchell. Taken together these two coefficients almost completely extinguish each other; and I can not help thinking that they should be allowed to do so entirely, and disappear from tables of physical constants.

Whatever may be thought of the accuracy of the value k at 0°; as finally obtained by Mitchell using his "cooled bar" method, it seems plain that the values 0.207 at 0° (Forbes) and 0.1509 at 0° (Mitchell) ought not to appear in the same table without an express statement that they were found from the same bar. Indeed the history of bar D goes far to show that the Forbes method is not well suited for the nicer problems of thermal conductivity, the uncertainty in estimating surface emissivity being too great.

We have not sufficiently definite data for a profitable estimation of the ratio between the thermal and electric conductivity in bar D.

STEWART.

R. W. Stewart also followed the method of Forbes, with some variations of detail, using a bar which he describes thus: "The iron bar was a ¾-inch square bar, about 4½ feet long, of ordinary commercial wrought iron, having its surface filed up and very lightly polished with black lead to secure uniformity of radiating power." "The density of the iron was found to be 7.556 at 0°

C." The specific heat was found by Bunsen's ice-calorimeter to be represented by the formula

$$C_t = 0.1095\,(1 + .00073t),$$

t referring to the centigrade scale.

The thermometers of Forbes were replaced by a single thermo-electric couple, made of "a good soft iron wire and German silver," each wire about 0.5 mm. in diameter. The depth of the holes bored in the bar to receive the thermo-electric junction was about 1.4 cm., the diameter about 0.1 cm.

"One end of the experimental bar was immersed in a vessel of melted lead maintained at a constant temperature, and the rest of its length was exposed to the air, but protected from draughts and external radiation by a wide trough of sheet zinc." The dimensions of this trough are not given, but from the figure shown it appears to have been about 27 cm. deep, the bar being suspended so as to hang about half way between the bottom and the top, which was not covered.

"In taking a series of observations of the distribution of temperature along the bar, the heating was allowed to go on for five or six hours, and then the deflections corresponding to each hole along the bar were observed, up and down the bar, time after time, until a set of perfectly constant and concordant readings were obtained."

"The distribution of temperature along the bars [copper as well as iron was studied] in the stationary state was determined by inserting one junction successively into the small holes drilled in the bar, while the other junction was maintained at a constant temperature[1] by inserting it in a hole in a short iron bar resting on the bottom of the zinc trough. The deflections obtained were, in this way, proportional to the difference of temperature between the several points on the bar and the temperature of the surrounding air. It was found necessary to carefully insulate the ends of the wires of the couple from one another just above the junctions, and from the bars in which they were inserted; this was done by filing down the

[1] "This temperature was indicated by a thermometer placed with its bulb in a hole drilled in the [short] bar close to the small hole in which the junction was placed. In no case was the variation of temperature more than a fifth of a degree. The bar was a short massive iron bar, not the one used for cooling experiments."

wires, inserting a thin slip of silk between them, and then whipping them around with a fine silk thread. The outer surface of the thread charred slightly at the higher temperatures, but not sufficiently to destroy its efficiency." "The rates of cooling of the bars at different temperatures were determined by heating a piece of each bar, about a foot long, in a sand-bath to a temperature higher than required, and observing its rate of cooling under the same conditions as those to which the experimental bar was exposed. For this purpose it was suspended in the position originally occupied by the long bar, the thermo-electric junction inserted in a hole drilled at its middle point, and the deflection of the galvanometer observed at regular intervals during the cooling."

Winkelmann quotes from the abstract of Stewart's work given in the *Proceedings* of the Royal Society. But in the *Transactions*, a mistake having been discovered, Stewart gives

$$k_t = 0.175\ (1 - .0015t).$$

I am of the opinion that little importance should be attached to the value of k obtained by Stewart and still less to his value of the temperature coefficient. A thermo-electric junction such as he describes, placed in a hole in the hot bar, but not in metallic contact with it, the greater part of the length of the wires being exposed to the air and the other junction being at a temperature near that of the air, would surely not have the temperature of the iron adjoining it. Moreover, we are told nothing about the location of the short bar carrying the colder junction except this, that it rested upon the bottom of the zinc trough—whether near the hot end or the cold end or the middle of the long bar, we do not know; but this one short bar was assumed to have the effective average temperature of the surroundings of the long bar and to hold the cooler junction at this same temperature.

Finally, the method of noting fall of temperature in the cooling bar, one foot long, by means of a single thermo-electric junction inserted at its middle point, is apparently inaccurate. The ends of the bar would certainly cool faster than the middle.

Near the end of his paper Stewart remarks, "Angström's method should be adopted in preference to Forbes'." Having now done

with researches by the method of Forbes, I return to the consideration of work done by his contemporaries.

Angström.

Angström used two bars of iron; the second, from which he obtained his best known results, was 117.8 cm. long and 3.5 cm. thick. I have found no description of its quality. Angström takes 0.8862 as the product of its specific heat by its density; but he uses precisely the same quantity for his other iron bar. It does not appear that he determined either the specific heat or the density.

Angström's general method of sending waves of temperature along the bar by alternate heating and cooling of one end, the remainder of the bar being exposed to the air, and noting the fluctuations of temperature at certain chosen points, is familiar to physicists and perhaps even more familiar to mathematicians. The mathematical discussion of the method, as given by Angström, treats specific heat and thermal conductivity as constants, it being assumed that the variation of these quantities, within the range of temperature fluctuations in the part of the bar studied, is too small to affect seriously the result arrived at. As to the validity of this assumption there has been discussion, which I do not propose to renew at present.

Whatever may be the merits of Angström's method, it is easy to show that he made near the end of his second paper[1] a large numerical error, the easy correction of which will bring his value of k for iron much nearer to the values obtained by most other investigators who have attempted to determine it.

The paper just referred to in Poggendorff contains the following record of data and experimental results:

Eisenstab.

No.	Period.	$\frac{k}{c\delta}$	Temp.	
1	32′	10.487	43°.4	Einfache Reihe: Therm. No. 2 u 3
2	32	10.429	43 .7	Doppelte Reihe: Therm. *A* und *B*
3	32	10.279	18 .9	

[1] Poggendorff, Vol. 118, p. 423, has a translation of the original paper.

This is followed, after a page or more devoted to the discussion of a similar record for copper, by a passage, quoted below, in which Angström professes to deduce a formula for k, as dependent on temperature, from the data which I have just given. A brief examination is enough to show that his formula, which has a negative temperature coefficient for k, cannot be derived from the numbers he refers to, which evidently give a positive temperature coefficient for k. Suspecting a mistake in the data as given in Poggendorff, I went to the original paper[1] and found the following table, which differs from that given above in one place of one number. We must therefore discard the data as given in Poggendorff, and consider whether the value given for k by Angström is consistent with the original data as here reproduced:

JERNSTÅNGEN.

No.	Period.	$\frac{k}{c\delta}$	Temp.	Anmärkningar.
1	32m	10.487	43°.4	Enkel serie; therm. no. II. o. III.
2	32	10.429	43 .7	Dubbel serie; therm. A o. B.
3	32	11.279	18 .9	" " "

The following discussion, by means of which Angström deduces his value of k, I quote from the article in Poggendorff, having compared the formulas in this discussion with those in the original passage and found them to be the same.

"Berechnet man den Werth von $\frac{k}{c\delta}$ aus den in der Tafel aufgestellten zwei letzten Bestimmungen für das *Eisen*, welche vollkommen vergleichbar mit einander sind, so erhält man

$$\frac{k}{c\delta} = 13.458\,(1 - 0.002874\,t)$$

und, wenn man setzt

$$c\delta = 0.8862$$

wird

$$k = 11.927(1 - 0.002874\,t).\text{"}$$

Now if we take the last two lines of the original data and calculate for them the value of $\frac{k}{c\delta}$ for 0°, we get 11.927. But this is

[1] Öfversigt af Kongl. Vetenskaps-Akademiens Förhandlingar, 1862, p. 24, Stockholm.

precisely the value which Angström gets for k at 0°. According to the data referred to by Angström, he should get

$$k_0 = 11.927 \times 0.8862 = 10.57;$$

and in general

$$k = 10.57\ (1 - .002874t),$$

for this revision requires no change in the temperature-coefficient which will be found perfectly consistent with the data.

The fact appears to be that Angström, having before him the quantity 0.8862 which he was presently to use as a multiplier, accidentally let it get in as a divisor, so that its final use as a multiplier merely gave back the value of $\frac{k}{c\delta}$, instead of giving the value of k.

In at least one other particular the calculations of Angström can profitably be revised. He treats the product $c\delta$ as a constant, using the same value for one bar at 0° as for another at 50°. But I shall now take the values of $\frac{k}{c\delta}$ which he gives as the results of experiments at 43°.7 and at 18°.9, apply to these the values of $c\delta$ which appear suitable to the temperatures, and work out thus values for k at 43°.7 and at 18°.9, and finally at 0°.

There can be no great error in taking 7.8 as the value of δ at all the temperatures considered, if Angström used good wrought iron, as in all probability he did. For the values of c I shall use numbers which are obtained by a combination of those given by Lorenz with those found by Naccari.

	Lorenz.				Naccari.		
Temp.	0°	50°	75°	100°	0°	15°	100°
Sp. ht.	0.1050	0.1107	0.1136	[0.1165]	[0.1080]	0.1091	0.1151

The numbers in brackets are my extrapolations. Then

$$c = \left\{\begin{matrix} 0^\circ \\ 0.1050 \\ 0.1080 \end{matrix}\right\} 0.1065 \qquad c = \left\{\begin{matrix} 100^\circ \\ 0.1165 \\ 0.1151 \end{matrix}\right\} 0.1158.$$

By interpolation

$$\begin{array}{cc} 18°.9 & 43°.7 \\ c = 0.1083 & c = 0.1106. \end{array}$$

Using these values of c, we get

$$k \text{ at } 43°.7 = 10.429 \times 7.8 \times 0.1106 = 8.999,$$
$$\text{“ “ } 18°.9 = 11.279 \times 7.8 \times 0.1083 = 9.528,$$

and by extrapolation k at $0° = 9.93$. The general formula now becomes

$$k = 9.93(1 - .0021t),$$

in the units employed by Angström—the centimeter, gram and minute. Reducing to the ordinary system by dividing by 60, we have

$$k = 0.1655(1 - .0021t).$$

Holborn and Wien, in the paper to which reference has been made, give as the result of Angström's work

$$k = 0.1628\,(1 - 0.002874\,t),$$

but do not tell in what way they have revised his calculations.

The value 0.1988, k at 0°, which both Winkelmann and Landoldt and Börnstein give in their tables on the authority of Angström, is obtained from his 11.927 by dividing by 60. The temperature coefficient of k from Angström's work is given by Winkelmann as—0.000517. I do not understand how this value was found. A little earlier, on p. 282, Winkelmann gives Angström's result, revised for the change of $c\delta$ with temperature and reduced to C. G. S. units, as

$$k = 0.1842\,(1 - 0.001562t),$$

but here again there is nothing to show just how the numbers are derived. One value of the temperature coefficient is a little more than three times as great as the other.

Angström recognized the fact that for a satisfactory comparison of thermal and electric conductivities both quantities should be found for the same piece of metal in the same state. Accordingly, he attempted to measure the electrical resistance, x, of his bars, but

encountered difficulties which baffled him, although he expressed the hope of overcoming them. Whether he finally succeeded I have not discovered. His results therefore tell us nothing directly in regard to the ratio $k \div \varkappa$.

Angström's method has not proved attractive to investigators in general. Tait tried it and gave it up. I am not aware that anyone except Angström has published results obtained by it for iron. Probably the very large value of k standing in the tables against the name of Angström has heretofore discredited his method. This consideration is now in great measure removed by the examination which has just been detailed. This objection, however, holds against all methods using temperature waves, that it is difficult for the ordinary reader, if not for every one, to see what effect will be produced in the result by small inaccuracies of theory or data. Such methods may give sufficiently accurate results, but they do not carry conviction.

Neumann.[1]

Neumann studied several metals. His whole published account of his work on these is contained in three pages; and the description is vague as well as brief. He used a method of variable temperature, heating one end of a bar or one section of a ring for a certain time and noting the changes of temperature after heating was stopped. Some features of his method can be seen in the work of H. Weber, which is presently to be described; for Weber avowedly followed Neumann as a guide, though perhaps with considerable deviations.

Neumann writes, "Les barres employées avaient 3 à 4 lignes de côté." The length is not given. "Dans quelques expériences j'ai aussi remplacé les barres par des anneaux." It seems not quite clear whether the results published were obtained from the bars or from the rings; but it is likely they came from the bars.

The specific gravity of the iron used was 7.74. Neumann gives 193 as the thermal conductivity of iron in the units employed, and says that this value can be reduced to the units used by Angström by multiplying by 0.0509. To reduce to C. G. S. units the

[1] Ann. de Chemie et Physique, Vol. 66, 1862.

193 should be multiplied by 0.0509 ÷ 60, which gives $k = 0.1637$, practically the same value which Landoldt and Börnstein put opposite the name of Neumann. I find nothing in Neumann to indicate the temperature for which his value of k is supposed to hold.

Neumann was especially interested in the ratio between thermal and electric conductivity, and he deduced comparative values of this ratio for the several metals which he used. He did not, however, determine the electric conductivity in absolute measure, or give any data from which we can now reduce it to that measure; so that the real ratio between the thermal and electric conductivities of the iron which he used cannot be found.

H. WEBER.

H. Weber "of Brunswick," not H. F. Weber as in Winkelmann, used the method of Neumann. The particular volume, No. 146, of Poggendorff, in which the original account of his work appears, is missing from the set which is at my command, and I have therefore had recourse to the translation of his paper which appeared in the *Philosophical Magazine*, vol. 44, 1872.

1. "Iron rod (annealed)," round; density 7.761; specific heat 0.1125 (temperature not given); length of bar 23.035 cm., diameter 0.75168 cm. "The density and the specific heat were specially determined, the latter according to the method proposed by Neumann."

After describing briefly the method of Angström, Weber says, "Neumann has now shown that the same problem can be treated in another way, and one more favorable for observation—and that it is more suitable for the determination of the two conducting-powers ["internal" and "external"] to subject not merely *one* end of a bar regarded as unlimited, but *both* ends of a bar of infinite length to the same periodic change of temperature in such a manner that when the two ends in the 0th period [really the *first* period of observations after the bar has been brought into a state of regular alternation] have the temperatures u_0 and u_1 they in the next following take the temperatures u_1 and u_0, in the 2d period (on the contrary) they are in the same state as in the 0th, and in the 3d as

in the 1st, etc." The temperature u_1 was that of steam, u_0 about 4°.6. The length of a period was 5 minutes.

Assuming for the purposes of mathematical discussion, that the specific heat, the density, the internal and external conductivities, are constant quantities, an assumption which Weber defends only as an unfortunate necessity, he proceeds to show that determinations of k, the internal conductivity, and h, the external conductivity, can be found from observations of the temperature of the air, the temperature of the middle point of the bar (which temperature should prove to be a constant), and the difference of temperature between two other properly chosen fixed points on the bar at various intervals during each period.

Thermoelectric effects, by means of wires soldered to the bar at the points mentioned, were used to measure the temperatures required. "A thin iron wire and a thin German-silver wire were soldered in the middle of it [the iron rod] * * * opposite to each other. The ends of these two wires were soldered to two copper wires," the points of junction being near together "in the surrounding air" at a point the temperature of which was read from a sensitive thermometer. At two other points, one of which was $\frac{1}{6}$ of the length of the bar from its end and the other $\frac{4}{6}$ of the length from the same end, "two German-silver wires were soldered to the iron bar * * * and their ends, at about 6 inches from the bar, were soldered to the two copper wires which led to the same galvanometer as the wires before mentioned." Readings of the deflections produced by this latter thermo-electric couple were taken at intervals of 15 seconds, and, as this deflection was changing rapidly during much of the time, a careful study of the characteristics of the galvanometer was necessary. The mean temperature of the air was about 5°.7; that of the middle point of the bar, 33°.1. The estimated mean temperature of the whole bar during a "period," of 5 minutes, was 39°.23, which, according to Weber, "can only be regarded as a rough approximation."

There is a tone of intelligence, frankness and thoroughness about the paper of Weber which inspires confidence. I cannot help feeling, however, that the description and discussion of the thermo-electric

devices is too meagre. How thick and how long were the "thin" wires soldered to the middle of the bar? How much solder was used in making the junctions, and how great was the thickness of solder between the wires and the bar? These seem to me important questions in a case where, as here, some of the points of attachment were rapidly varying in temperature and all were much above the temperature of the room. It is unfortunate that Weber did not make such variations in his thermo-electric apparatus as to remove reasonable doubts concerning its accuracy.

On the other hand we feel somewhat reassured by the fact that he did vary considerably the surface condition of the bar, without finding any corresponding important change in the value derived for the thermal conductivity.

After giving a series of values obtained from "even periods," which agree well among themselves, and a corresponding self-accordant series from "odd periods," he says, "If we take the mean of the values of K [the internal conductivity] and H [the external conductivity] given by the even periods, and likewise of those derived from the odd periods, we obtain:

$$K = 15.14, \qquad H = 0.00266,$$
$$K = 14.56, \qquad H = 0.00266."$$

The difference between "odd" and "even" is attributed to "want of absolute coincidence of the soldering-places with the points $x = \frac{1}{6}l$ and $x = \frac{4}{6}l$." For the mean we have

$$K = 14.85 \qquad H = 0.00266.$$

"The surface of the iron bar had not the highest polish. In order to try whether the quality of the surface exerted a perceptible influence on the value of K, the previous experiments were repeated with the same iron rod after its surface had been evenly coated with soot from a gas flame. The thickness of the coating was such that the metallic surface was just perceptible through it. Here the duration of the periods amounted to 10 minutes, in order to make the

observations in even and odd periods alternately, not consecutively as before." The mean results from the iron thus coated were

$$K = 14.79 \qquad H = 0.00328,$$

an extremely satisfactory agreement for K, with the previous result.

It is unfortunate that the temperature at which the specific heat was found is not given. The value used, 0.1125, seems rather high for the mean temperature of the bar. An error of two or three per cent. may occur here, making the value obtained for K too large by that amount.

Weber's values of K and H are expressed in terms of millimeters, milligrammes and seconds. To reduce to C. G. S. units we must divide K by 100 and H by 10. We are concerned with K only, from which we get

$$k = 0.1485,$$

as given by Landoldt and Börnstein and by Winkelmann. This is referred to the mean temperature of the rod, about 39°.

Weber found the ratio of the thermal conductivity to the electric conductivity, which henceforth I shall call the ratio $k \div x$, to be 2458×10^4 at 44°.3C, in the units which he used. Reduced to the C. G. S. system this ratio becomes 2458.

L. Lorenz.[1]

The iron used by Lorenz appears to have been exceptionally pure. It had a high density, 7.828 at 0°, and an electric conductivity greater than Landoldt and Börnstein quote for any other specimen of iron.

Lorenz gives from his own observations on this iron

Sp. Ht.	Elect. Cond.
$C_0 = 0.1050$	$x_0 = 10.374 \times 10^{-5}$
$C_{50} = 0.1107$	$x_{100} = 6.628 \times 10^{-5}$
$C_{75} = 0.1136$	

His bar was 30 cm. long and 1.5 cm. in diameter.

[1] Wied., N. F., 13, pp. 422 and 582, 1881.

In his main experiments Lorenz used two methods. One was that of Forbes with various improvements. The other, which he considers the more exact, consisted in measuring the time rate of increase of mean temperature throughout a certain part of a bar, with a known difference of temperature gradient at the ends of the portion considered, and with a surrounding jacket kept at a known fixed temperature by flow of cold water or steam. Moderate differences of temperature between different parts of the bar and between the bar and jacket were used. The temperature measurements were made by means of thermo-electric junctions, usually of copper and German-silver, but sometimes of copper and iron. Heat was brought into the bar by end contact with a bar of copper kept hot by means of a lamp. Of course it was necessary to know the density of the bar and its specific heat at various temperatures. Careful observations to determine these quantities were made upon the bar itself or upon a portion cut from it.

It is impossible to read the papers of Lorenz on thermal conductivity without being impressed by the thoroughness of his work and the probable accuracy of his results. But his method as a whole does not strike one as simple or easy to carry out, and there is one detail of the apparatus which suggests to me the possibility of considerable error. The thermo-electric junction commonly used consisted of a copper wire 0.01 cm. thick and a German-silver wire 0.03 cm. in diameter soldered together end to end in a straight line. This junction rested within a hole 0.04 cm. diameter bored straight through the bar from side to side, and both wires were insulated from contact with the metal of the bar, the German silver within the hole being covered with a thin wrapping of silk for this purpose. For the purpose of finding the temperature gradient leading heat into or out of the parts considered, "thermo-electric double elements were used which consisted of short German-silver wires with both ends soldered to copper wires." Now it seems probable that the ends of any one of these German-silver wires would, under the circumstances described, differ decidedly less in temperature than the parts of the bar at the two holes connected by the wire. This objection must have occurred to Lorenz, though he does not, so far as I have observed, mention it. It is easy to see that error from this defect of

apparatus would in some measure eliminate itself, since it is the difference of two temperature gradients which enters into the calculations. Moreover, Lorenz states that he sometimes used copper-iron thermo-electric junctions, and sometimes junctions made by copper wires joined directly to the bar, without finding any material difference in the results obtained. Finally, it is to be said that the Forbes method, which Lorenz used for checking the results obtained by his first method, gave nearly the same values for thermal conductivity in most cases. The agreement in the case of iron was especially good, the Forbes method giving a result about 1½ per cent. smaller than the other. It is true that similar errors may affect both methods as applied by Lorenz.

The original method used by Lorenz was particularly well designed for giving the temperature coefficient of k; and the value which he found for this coefficient would be entitled to much consideration, even if it should appear that the values which he found for k were somewhat erroneous.

Lorenz found, by his preferred method, for iron

$$k_0 = 0.1665, \qquad k_{100} = 0.1627,$$

in C. G. S. units.

The temperature coefficient from these values is 0.0002282.

Landoldt and Börnstein report k and its temperature correctly from Lorenz; but Winkelmann in deducing the temperature coefficient forgets to divide by k_0.

The ratio $k \div x$, as found by Lorenz for his iron bar at 0°C., is 1605.

BERGET.[1]

Berget made first a determination of the thermal conductivity of mercury in absolute measure, and afterward found the thermal conductivity of various solid metals, including iron, by comparison with the mercury. He found the gradient of temperature in a vertical column of mercury, of which the upper end was exposed to steam and the lower end was kept cool by melting ice. A "guard ring" of mercury, exposed to the same terminal temperatures as this

[1] Compt. Rend., 1887–'90. Journal de Physique, Vol. 7, p. 2, 1888, and Vol. 9, p. 135, 1890.

column, surrounded the column and prevented lateral escape of heat. The amount of heat transmitted by the shielded column was calculated from the amount of ice melted at its lower end, this latter quantity being found sometimes by use of a Bunsen ice-calorimeter, sometimes by weight. The temperature gradient was measured by means of thermo-electric couples, formed by iron wires leading through the guard cylinder into the interior column, with which they were in metallic contact.

The self-consistency of the results which Berget obtained for mercury is marvelous, but not greater than the admirable simplicity and directness of his method seems capable of giving. There was no need of determining specific heat or "surface conductivity."

In working with solid metals Berget superposed a column of mercury upon a column of the solid, each surrounded by its "guard ring," found the gradient of temperature in each by thermo-electric means after a stationary condition was reached, and then deduced the conductivity of the solid from that of mercury by the simplest of calculations.

The whole account of his work given by Berget is brief, and some details of apparatus or procedure are described less fully than the reader could desire; but the general method is so excellent that one can have little doubt concerning the accuracy of all parts of the investigation. It is therefore the more to be regretted that Berget has not told us the degree of purity, or even the specific gravity, of the metals which he studied. Perhaps it is not yet too late for this omission to be made good.

He determined, for solid metals, the mean thermal conductivity between 0°C. and 30°C. and declared its value to be, for iron, 0.1587.

He found the mean electrical conductivity of the same bar of iron to be, between 0°C. and 30°C., 9.41×10^{-5}.

The ratio of the mean values of the two conductivities between these limits of temperature is therefore, according to Berget,

$$k \div x = 1687.$$

This may be taken as equivalent to

$$k_{15} \div x_{15} = 1687.$$

BEGLINGER.[1]

Probably the broadest piece of work ever done by one person upon the thermal conductivity of iron is that of W. Beglinger, who determined the density, specific heat and thermal conductivity of 52 pieces of iron, including steel and cast iron, of many varieties. The following passages freely translated from his own descriptions will give an account of the general method and arrangement of apparatus.

"A broad cylinder, which in all points had the same initial temperature N, was from a determined moment, which we take as the zero point of the time, subjected to a continuous cooling by keeping its base continually at the temperature 0°, while the remainder of its surface was allowed to give off heat into a space kept likewise at the constant temperature 0°. The time-rate of fall of temperature at any point of the cylinder can be arrived at by calculation; and after certain simplifications of the expression thus obtained for the temperature, there results the method for the determination of the internal heat conductivity." The method thus indicated is credited to H. F. Weber,[2] who had applied a somewhat similar method to the study of heat conduction in several metals[3] about 1880. "The temperature was measured thermo-electrically. Since it would not do to break the continuity of the material by means of small canals, one junction of the thermo-element was placed at the middle of the upper end surface [of the cylinder], the other junction kept at the constant temperature 0° [so-called] of the cooling water. The thermo-electric current was led through a galvanometer of such a character as to permit the variable electromotive force to be followed exactly after the lapse of a few seconds." * * * "From a given moment, after the cylinders had been heated, its lower end surface was played on by a stream of water 3 cm. thick from the public water supply (having a pressure about 7 atmospheres), while care was taken that the upper end as well as the curved surface of the cylinders should not be touched by the water."

"In the center of the upper end surface [of the cylinder] a drill hole 0.2–0.25 cm. broad and 0.15 cm. deep was filled with a piece

[1] Verhandlungen des Vereins zur Beförderung des Gewerbfleisses, vol. 45, 1896, pp. 33–61.

[2] Berliner Monatsberichte, 1880, and Wied. Ann., Bd. 13.

[3] Vierteljahrsschrift der Naturforschenden Gesellschaft in Zurich, vol. 25, 1880.

of soft copper. In this was bored a fine hole in which the junction [of the thermo-element, of thin iron and German-silver wire] could be easily and securely placed."

The narrowest cylinders used by Beglinger had a diameter of nearly 6 cm.; the greater number had a diameter of 15.8 cm. or more. The least length was 4.44 cm.; the length of the greater number ranged from 6.5 cm. to 8 cm.

Each cylinder when in use was mounted on, or rather in, a broad thick supporting plate of iron, having at its center a hole widening conically toward the upper face and just wide enough at the bottom face to admit the cylinder. The lower end surface of the cylinder was made flush with the lower surface of the plate, being supported in that position by three small lugs attached to the under face of the plate. There could be side contact between cylinder and plate only along a strip ½ mm. high. The narrow space between the two was filled with a cement consisting of yellow wax and "Kolophonium." Above the cylinder was placed on the plate a double-walled cap of sheet copper containing water of the same temperature as the other cooling water. The water jet, about 3 cm. wide, was directed against the middle of the base of the cylinder from a distance of 3 or 4 cm. with very great force, and "erst am Rande des Gestelles [support] in seiner Bewegung in horizontaler Richtung gehemmt, nahm es seinen Weg nach unten." At the maximum this stream delivered about 3.7 liters of water per second with a velocity of 5.3 meters per second. A considerable reduction of the flow was accompanied by a perceptible loss of effectiveness of the stream.

The warming of the cylinder was effected by means of a Bunsen burner; and it lasted from 3 to 5 minutes, at times as much as 10 minutes. After the operation the under surface of the cylinder was always carefully cleaned and the water jet was put into position. Two or three minutes were thus allowed to elapse, in order that for the subsequent cooling it might be assumed that the initial temperature was everywhere the same. The warming was observed by means of the galvanometer, and "im Allgemeinen wurde nicht über 40° Temperaturdifferenz hinausgegangen." I think 40° is here a mistake for 4°; for I find later, as a typical case, "Kühlwassertemper-

atur 3°.3 C." * * * "$\bar{n} = 2°.0$; also gilt das Resultat für die Temperatur 5°.3 C."

As the "external" conductivity plays a certain part, though a subordinate one, in the cooling, certain direct observations upon rate of cooling by external conductivity alone were made.

In some cases the effect of removing the thermoelectric junction from the middle of the cylinder end to an excentric position was tried.

Each cylinder was tested in both of its upright positions; that is, the face which had been the base in one set of observations was made the top in another set; this gave a rough test of the homogeneity of each cylinder, which test all of the wrought-iron cylinders except one and all of the steel cylinders except one bore well. But with 14 out of 31 cast-iron cylinders the values of k obtained from the two positions differed from each other by 2% or more.

For the determination of its specific heat each cylinder was heated in a water bath to "30, 40 oder 50°," from which it was after a time quickly transferred to the calorimeter. The giving out of its heat in this calorimeter occupied from 4 to 8 minutes.

Beglinger uses the minute as his unit of time. His values of k are, therefore, to be divided by 60 in order to reduce them to the C.G.S. system, and the reduction is made in the following table, which gives the results of his work with malleable iron (Schmiede-eisen):

Schweisseisen.					
No.	l	$2R$	ρ	c	k
	cm.	cm.			
1. Schweisseisen, Gerlafingen	7.387	15.91	7.835	0.1110	0.1502
2. Sandwyk-Eisen	6.992	19.96	7.884	0.1104	0.1492
3. Siegener Schweisseisen	6.987	19.96	7.803	0.1107	0.1329
4. Schweisseisen, Gerlafingen (E.)	6.982	19.96	7.812	0.1115	0.1279
5. Frischfeuereisen, Gerlafingen	7.447	20.05	7.693	0.1112	0.1263
6. Packeteisen "	7.285	20.05	7.806	0.1110	0.1262
7. Hayange, No. 2, gewalzt	6.970	15.92	7.521	0.1134	0.1078
8. Hayange, No. 2, geschmiedet	6.987	15.91	7.550	0.1122	0.1112
Flusseisen.					
9. Flusseisen, Gerlafingen	7.275	20.05	7.849	0.1108	0.1346
10. Flusseisen	6.045	15.87	7.657	0.1125	0.1241

l = length. $2R$ = diameter.
ρ = density. c = specific heat.
k = thermal conductivity.

Beglinger does not tell, as a rule, for what temperature his values of c or of k were determined; but from various remarks it seems probable that the temperatures for k lie between 5°C. and 20°C. The mean temperatures for which c was experimentally determined probably lay ten or fifteen degrees higher. Whether the values of c, as given above, are reduced to the lower temperatures for which k holds, we are not, I believe, directly told; but it appears as if these values of c were used in finding k. The mean of the values given for c is about what Naccari and also Lorenz would give for the specific heat of iron at 50° C.

Without questioning the great value and merit of Beglinger's work, one may suspect his results for k to be affected by considerable errors. For example, the description of the method of warming the cylinder leaves it very doubtful whether its temperature was everywhere the same at the beginning of the cooling. Moreover, it is even possible to doubt whether the lower face of the cylinder, in spite of the great size and velocity of the water stream directed against it, had everywhere the temperature of the water in the stream. The parts directly attacked by the full force of the stream would, perhaps, soon attain and keep a temperature very nearly the same as that of the stream itself; but other parts would probably be less affected. We might, therefore, expect narrow cylinders to be cooled somewhat more rapidly, other things being equal, than broad cylinders. As to the possible action along the curved surface of the cylinder Beglinger remarks: "Es ist zu bemerken, dass aus der Erwärmung des Gestelles [during the warming of the cylinder by means of a Bunsen burner] kein Fehler entstehen konnte; ebensowenig ist ein Einfluss der Kittschicht, trotz vielfacher Modifikationen konstatirt worden." It is to be remarked, however, that if there is any flow out through the cement layer during the cooling, this flow would hasten the cooling more, other things being equal, in narrow cylinders than in broad cylinders. We find here, then, two possible influences tending to make k appear greater in narrow cylinders than in broad cylinders. Reasoning in this way, I was curious to see whether the results, as given by Beglinger, would give any indication of such a result. It happens that he used 11 pairs of cast-iron cylinders, the individuals of each pair

being of the same material and differing, so far as was known beforehand, only in the diameter, which was about 6 cm. for one and 16 cm. for the other. Taking mean values I find

	ρ	c	k
For broad cylinders,	7.102	0.1152	0.1192
For narrow cylinders,	7.093	0.1159	0.1225

The mean k found for the narrow cylinders is, therefore, about 2.5% greater than the mean k found for the broad cylinders; and as the mean density and mean specific heat are nearly the same for one set as for the other, it seems probable that the apparent difference in the mean values of k is due to some fault in the method of experimentation.

This is not a very grave criticism of the work of Beglinger, which from its scope was necessarily somewhat rough in details; but it should be borne in mind hereafter, if there should be a disposition on the part of any one to discredit the values obtained by others on the ground that these values do not agree with any of those given by Beglinger. The maximum value of k which he found for wrought iron is 0.1502, which is a very little smaller than the value which I have found for a less dense piece of iron, about 5% less than the value found by Berget, and 10% less than the value found by Lorenz for iron of very nearly the same density, as Beglinger's iron.

Beglinger's results seem to show that, in the case of malleable iron, density is an important, though by no means the sole, factor in determining the value of k. The greatest value of k was not found in the most dense piece, No. 2, nor the least value of k in the least dense piece, No. 7; and yet, when the values of k for the ten pieces of malleable iron are plotted as ordinates with the densities as abscissas, it appears that an increase of 1% in the density is accompanied by an increase of several per cent. in the value of k, and there is an indication that the rate of increase of k rises with the increase of ρ. The other variables upon which k in soft iron depends are, according to Beglinger, very obscure. He calls attention to the fact that k in cylinder No. 1, which came directly from the iron-works, was about 15% greater than k in No. 4, a cylinder of the same material which came through a commercial

firm. The density and specific heat were about the same in one of these cylinders as in the other. It seems a pity that serious effort was not made, by dissection and minute examination of these two cylinders, to discover the cause of their great difference in k.

It may be well to add a few words concerning the results of Beglinger for steel and cast-iron.

The 11 cylinders of the steel group were all "Flussstahlsorten." In these

ρ varied from 7.84 to 7.92,
c " " 0.1110 to 0.1135,
k " " 0.1327 to 0.0940.

There was among these no apparent connection between ρ and k.

Among the 11 cylinders four pieces are numbered twice each, once in the soft condition and once in the hard condition. "In 3 Fallen hatte der gehärtete Cylinder ein kleineres k als der weiche, aber nur um 11, 5 und 6% ; in eniem Falle hatte sogar der gehärtete Cylinder ein um 2% grösseres Leitungsvermögen." "Die Ergebnisse für das Härten bestätigen die Resultate des Herrn Kohlrausch nicht." In fact, Beglinger comes to the conclusion that hardness and softness in steel, whether due to its mode of manufacture or to subsequent treatment, has comparatively little influence on k. It is to be observed, however, that Beglinger used pieces of steel about 4.5 cm. thick, and, as he does not describe his method of hardening them, it may well be doubted whether he succeeded in making them very hard throughout.

Within the cast-iron group of 31 cylinders,

ρ varied from 6.849 to 7.217,
c " " 0.1120 to 0.1210,
k " " 0.0932 to 0.1533.

Here, as in steel, there is no apparent connection between ρ and k. It seems to be a matter of mere chance whether a very dense piece of cast iron has a high, low or medium thermal conductivity. In the eleven pairs of cast-iron cylinders already mentioned, the individuals of each pair being ostensibly of the same material, Beglinger found

always a difference of k between these individuals, the smallest difference being less than ¼%, the largest 21%.

Beglinger gives the chemical analysis of none of his cylinders, and expresses a doubt as to whether such analysis would clear up the differences observed, in view of the comparatively small effect produced by the presence of a large amount of carbon. "Der gebundene Kohlenstoff drückt beim Gusseisen das k etwas hinunter im Beispiel des Cylinders No. 40 gegenüber No. 33, wo der Kohlenstoff zum grössten Theil in Form von Graphitblättchen ausgeschieden ist." "Ueber den Einfluss von Mangan, Silicium und Schwefel etc., auf das Wärmeleitungsvermögen von Stahl und Eisen fehlt jeder Anhaltspunkt."

I find from the values given by Beglinger:

for 10 pieces of soft iron the mean $k = 0.1300$,
" 11 " " steel " " " $= 0.1100$,
" 31 " " cast iron " " " $= 0.1175$.

HALL.

The general method which I have followed in measuring the thermal conductivity of a plate of wrought iron is the same as that used by Mr. Ayres and myself in our work on the thermal conductivity of cast iron.[1] Certain changes of apparatus or procedure, the most important being the substitution of platinum thermometers for thermoelectric junctions in measuring the change of temperature of the water passing over the disk, will be described in the Proceedings of the American Academy; but the character of the iron used and the results obtained will be given here.

The metal was Yorkshire wrought iron, recommended to me by an engineer friend of much experience as the softest wrought iron to be found in the Boston market. At the place of purchase the metal was described to me as containing 99.7% iron and no carbon. Chemical analysis made at my instance showed

iron	99.93%,
carbon	0.059%.

[1] Proceedings of American Academy of Arts and Sciences, Vol. 34, p. 283, 1899.

The values which I find for the thermal conductivity, k, of this iron are, at

28°.2C.	0.1528,
58°.3C.	0.1514,

if the specific heat of water at each of these temperatures is called 1. This would give for the temperature coefficient 0.0003, very nearly.

If the values of k are revised in accordance with the values proposed by Winkelmann[1] for the specific heat of water at the given temperatures, they become at

28°.2C.	0.1513,
58°.3C.	0.1511,

and the temperature coefficient deduced therefrom will be too small to be worth writing down, 0.0000?, let us say.

But the recent work of Callendar and Barnes[2] gives for the specific heat of water

0.9992	at 25°C.
0.9987	at 30°C.
0.9992	at 55°C.
1.0000	at 60°C.

If these values given by Callendar and Barnes are adopted as correct, my first values of k will stand almost without change; and I shall therefore leave them for the present without correction for variation in the specific heat of water.

My value for the temperature coefficient, 0.0003 or a little less, is, so far as it goes, a corroboration of the substantial accuracy of the temperature coefficient found by Lorenz, 0.0002282, although it may be doubted whether the last three figures of this number are of much significance. This agreement is eminently satisfactory to myself; for a comparison of the work of Lorenz with that of other investigators has convinced me that his value of the temperature coefficient is entitled to an especial degree of confidence.

[1] Part 2 of Vol. 2, p. 340.
[2] This REVIEW, April, 1900.

Measurements of the electrical resistance of the iron were made on 9 cylinders, each 2 cm. long and about 0.23 cm. in diameter, cut from the same great bar as the disk on which the measurements of k were made. The length of the cylinders, like the thickness of the disk, was taken parallel to the length of the bar; and the cylinders were cut from a part of the bar adjacent to that from which the disk was cut. The extreme difference in the specific resistances of these cylinders was apparently about 5 per cent. The mean specific resistance was found to be 12240 at 18° C. The mean specific conductivity, x, at the same temperature would, therefore, be 817×10^{-7} C. G. S.

Summary and Discussion.

In accordance with the preceding exposition I have made the following table of results for wrought iron, in which ρ = the density, x = the electric conductivity, k = the thermal conductivity:

Observer.	ρ	$x \times 10^7$	k
Method of steady flow with "external conduction."			
Forbes,	7.79	?	0.207 (?) at 0°C. (see Mitchell).
Mitchell,	7.79	?	0.1509 (?) at 0°C. (sp. ht. uncertain).
Stewart,	7.556	?	0.175 (?) at 0°C.
Methods using waves or oscillations of temperature.			
Angström,	?	?	0.1655 (?) at 0°C. (sp. ht. uncertain).
Neumann,	7.74	?	0.1637(?) at ? (account too brief).
H. Weber,	7.761	604 at 44°C.	0.1485 at 39°C.
Methods of rise or fall of temperature with internal and external conduction.			
Lorenz,	7.828	1037.4 at 0°C.	0.1665 at 0°C.
Beglinger,	7.74	?	0.130 (?) at ? (method rough).
Method of steady flow with guard ring or jacket.			
Berget,	?	941 at 15°C.	0.1587 at 15°C.
Hall,	7.785	817 at 18°C.	0.1528 at 28°C.

Temperature coefficient of k.

Lorenz, $a = -0.0002282$.

Hall, $a = -0.0003$ or slightly less.

The only two values here given for a were obtained by very different methods, which, however, have this very important feature in common, that each of them used precisely the same piece of

metal in finding the low temperature value of k as in finding its high temperature value, the whole apparatus being used at two different levels of temperature, with little or no relative change within it in passing from one level to the other. In the Forbes method of finding a, followed by Mitchell and Stewart, the high temperature value of k is found at one part of a bar and the low temperature value at a different part, where the quality of the metal may not be quite the same. For this reason, as well as for others which will be apparent to any one reading the preceding discussion of work by the method of Forbes, I have retained none of the values of a obtained by that method. The value to be derived from the data given by Angström seems also too uncertain for a place in this summary.

If we take -0.00025[1] as the value of a in wrought iron of high grade, I believe that we may have much confidence in the ciphers and some confidence in the first digit.

In four cases we have both k and x in C. G. S. units. Reducing to 0°C., using -0.00025 as the value of a and $x_0 = x \div (1 - 0.0051t + 0.000013t^2)$ as the temperature formula for electrical conductivity, we get in these four cases

Observer.	ρ	x	k	$k \div x$
Lorenz,	7.828	10374×10^{-6}	0.1665	1605
Berget,	?	10160 "	0.1593	1568
Hall,	7.785	8958 "	0.1539	1716
H. Weber,	7.772	7540	0.1500	1989

The mean of the four values here given for k is 0.1574. The mean value deduced by Holborn and Wien was 0.156 at (?)°C.

It is plain that diminution of density is here accompanied by fall of both x and k. It will be remembered that Beglinger's results also, for soft iron, indicated a fall of several per cent. in k with a fall of one per cent. in ρ. It would be unwise, however, to draw definite numerical conclusions from the numbers before us; for all the values of x and k are in some degree uncertain, and in the case of Weber's iron even the ρ is a little dubious; for he does not tell the temperature for which ρ is 7.761, and I have assumed that it

[1] Holborn and Wien, *loc. cit.*, retaining the values of a given by Mitchell and Stewart, get, as the most probable value, $a = -0.001011$.

was 39°C., which he gives as the mean temperature for which he determined k. We should be in better position for speculations if we knew the value of ρ in the iron used by Berget. The x and k for this iron seem to require a high density.

Although k appears to increase rapidly with increase of ρ, x increases still more rapidly, so that, with one exception, we find $k \div x$ to decrease with increase of k. This exception may be due to entirely obscure causes lying in the difference of quality of the iron used by Lorenz and Berget respectively, or it may be due to errors of measurement by one or both of these investigators. To determine this ratio within 1 % for any piece of iron would be a considerable achievement. It is worth while to inquire what values of this ratio were obtained by Lorenz and by Berget for the other metals which were examined by both of them. Brass being omitted as a too uncertain quantity, these metals were copper, tin, lead and antimony. Berget's results being given for 15°C., we must reduce them to 0°C.; and for this purpose can not do better than to take the temperature coefficients found by Lorenz. Using these we get for the ratio $k \div x$ at 0°C.

	Lorenz.	Berget.
Copper,	1574	1516
Tin,	1635	1727
Lead,	1627	1532
Antimony,	2011	1629

Thus we have, including iron, four cases out of five in which the value of $k \div x$ found by Berget was less than that found by Lorenz. I am, therefore, inclined to attribute the exception above noted, in the column $k \div x$ for iron, to errors of measurement, and to hold it as a rule that in iron the ratio $k \div x$ decreases with increase of k.

In conclusion I have to make the following suggestions:

1. That every one who undertakes to determine the thermal conductivity of any metal should determine also its electrical conductivity and thermoelectric quality, and should give in general the most definite attainable account of its physical and chemical properties.

2. That every one should have regard not merely to the probable accuracy of his method but also to its convincingness, lest his re-

sults, however accurate, may be received with doubt and so prove ineffective.

3. That the general methods used by Berget are peculiarly simple, direct and convincing; and that his probably very accurate determination of k for mercury puts at the disposal of all other investigators a standard substance by comparison with which they may, using his guard-ring method, measure the conductivity of other metals with far less labor than if they undertook independent absolute determinations.

A striking example of the uncritical use of old data relating to thermal conductivity is furnished by the paper of Liebenow referred to at the beginning of this article. Liebenow derives from his theory the following formula for the thermo-electromotive force in any metal:

$$\frac{dE}{dT} = \pm 2.04 \sqrt{\frac{RL}{T}},$$

where dE is the electromotive force in volts,

dT " difference of temperature in degrees C.,
R " specific resistance in ohms,
L " thermal conductivity,
T " absolute temperature.

He then says, " For copper one finds accordingly at 15° C., if one takes 0.8 as the specific thermal conductivity of copper,

$$\frac{dE}{dT} = \pm 2.04 \sqrt{0.8 \times 0.000001635 \div 288} = \pm 0.0001375 \text{ volts."}$$

Why Liebenow took the value 0.8 he does not say. The values given by Winkelmann on the authority of various observers range from 0.6296 to 1.11. But having taken this value for copper he follows the curious course of calculating the thermal conductivity for iron by multiplying 0.8 by the value which Wiedemann and Franz found for the thermal conductivity of iron as compared with copper, as if there had been no improvement on the work of these observers during the past forty-five years. The electric conductivities

are taken from Matthiessen's values. Accordingly Liebenow gets for iron

$$\frac{dE}{dT} = \pm 128.2 \text{ microvolts,}$$

"and one gets for the iron-copper element -9.3 microvolts [that is, $128.2 - 137.5$]; which agrees very well with observations."

To show how much importance Liebenow attaches to the case of iron and copper, I will quote one more passage. "Since the electric stream in the copper-iron element, under 276°, flows from copper to iron at the warm junction, though the electromotive force of the copper is in this case larger than that of the iron, it follows that the direction of these forces is opposite to that of the heat flow; that is, the positive electricity is in these metals, with unequal temperature, driven toward the warmer places. Moreover, since all metals investigated by Matthiessen give, in combination with copper, smaller electromotive forces than 137.5 microvolts, one must conclude that all metals when unequally heated become electrically *positive* at the warm end."

But let us see how the argument would run if we were to use the results obtained by Lorenz and by Berget, both excellent and, as compared with Wiedemann and Franz, recent experimenters.

From the data given by Lorenz we get for copper at 0° C.

$$\frac{dE}{dT} = 2.04\sqrt{\frac{RL}{T}} = 2.04\sqrt{\frac{k}{xT}10^{-9}} = 0.0001549 \text{ volt,}$$

and for iron at the same temperature,

$$\frac{dE}{dT} = 2.04\sqrt{\frac{k}{xT}10^{-9}} = 0.0001564 \text{ volt.}$$

Thus we find $\frac{dE}{dT}$ greater for iron, the opposite of what Liebenow finds. At 15° C., the temperature used by Liebenow, the excess of $\frac{dE}{dT}$ for iron would be a little greater than at 0° C.

From Berget's data we get at 15° C. for copper

$$\frac{dE}{dT} = 2.04\sqrt{\frac{1.045}{651300 \times 288}} = 0.0001519 \text{ volt,}$$

and for iron at the same temperature,

$$\frac{dE}{dT} = 2.04\sqrt{\frac{0.1587}{94100 \times 288}} = 0.0001561 \text{ volt.}$$

Here again, $\frac{dE}{dT}$ is greater for iron than for copper.

However sound Liebenow's general theory may be, it seems plain that his computations should be revised.

CAMBRIDGE, May 12, 1900.

SPARK-LENGTH OF AN ELECTRIC INFLUENCE MACHINE, AS MODIFIED BY A SMALL SPARK FROM THE NEGATIVE SIDE.

By W. J. Humphreys.

ABOUT ten years ago I noticed that the discharging distance between the poles of an ordinary Toepler machine could be very greatly increased by the aid of small sparks, taken by the hand or otherwise, from the negative pole, or from any part of the machine in metallic contact with it; and also that this property was peculiar to the negative side, no such effect being produced by sparks taken from any of the positive parts.

Naturally I supposed that a description of this phenomenon, so easily and in fact often accidentally obtained from so common a machine, was to be found in the journals and larger treatises, but I have not been able to find any reference to it. I therefore venture to publish a short account of my experiments along this line, trusting that the results, if not new and interesting to all, may at least be so to many.

For the sake of convenience and clearness I refer to the accompanying sketch, in which *J, J*, are the two small leyden jars usually on electrical influence machines, *W* the wire connecting their outer coatings, *A* and *B* the discharge balls. *C* and *D* connect, one with the positive the other with the negative comb of the machine.

Let the machine be run continuously, and let the distance between *A* and *B* be gradually increased till the sparks cease to pass. If a small spark is now drawn from any part of the machine metallically connected with the *negative* pole, the dilectric between *A* and *B* will in general break down and a spark of full magnitude pass between them.

In this way the sparking distance may be increased anywhere up to seventy-five per cent. or even more, the extent of increase depending on many things as will appear from the experiments described below.

The experiments were usually made with the machine in constant action, but this was only a matter of convenience as the discharges between the poles could still be forced, by the aid of a small spark from the negative side, after the machine had come to rest, but of course before the potential had dropped very greatly.

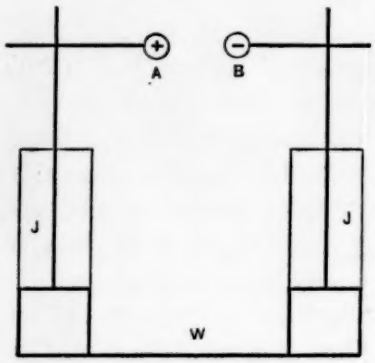

Fig. 1.

The phenomenon has been tried, and with uniform success, with several machines; among them an old type Holtz, Toepler and Wimshurst machines. Most of my observations however have been made with a two-plate Wimshurst machine, the plates being twenty inches in diameter, of ebonite and furnished with metallic sectors.

When the poles were equal in polish and otherwise it was, as one would expect, a matter of indifference which was positive and which negative, the forced spark being obtained equally well in each case.

The phenomenon has been tested under quite a number of conditions—some of which are the following. Where no statement to the contrary is made, the condensers belonging to the machine were used, and both poles kept polished.

1. Roughened negative pole. Results never good; the negative pole lost its charge so rapidly in the form of a brush that it was impossible to obtain sparks of any considerable length.

2. Polished negative pole. Results generally very good.

3. Condensers of very small capacity. Increase in spark gap slight.

4. Condensers of large capacity. Spark gap not much increased.

5. No condensers. Spark gap not affected by spark from either pole.

6. Condensers belonging to machine, and polished negative pole. Results generally excellent.

7. State of the atmosphere such as to prevent high potential, machine giving only short sparks. Results less pronounced, the poorer the working of the machine.

8. Condition of the atmosphere such as to cause unusually long sparks. Increase of spark-length ordinarily not very great.

9. Working of machine such as to give sparks of medium length, from eight to twelve centimeters with the Wimshurst machine. Increase of spark-length most pronounced, often nearly doubling the distance between the poles.

10. Poles separated very widely. In this case a spark could not be made to pass the whole distance, but each time a small spark was taken from the negative side a discharge passed from the positive pole and lost itself along many branches into the air. Nothing of this kind happened at the negative pole when a similar spark was drawn from the positive side.

11. Discharge poles removed some distance, about seventy centimeters, from the revolving disks. Results the same as when the poles were in their usual positions.

12. Outsides of condensers connected by metal rod. Results excellent.

13. Outsides of condensers connected by secondary of a large induction coil. Increase in sparking distance still very pronounced, but volume of spark diminished.

14. Outside of condensers connected by a wet string. Increase in sparking distance still decided, but volume of spark greatly diminished.

15. Condensers completely insulated from each other. Outsides temporarily grounded or not, but finally left insulated. In this case there was not the slightest indication of a spark on taking small discharges from either pole.

Various other arrangements were tried, but probably these are the most important, and from them it may be gathered that if the poles of an electrical influence machine be separated beyond their sparking distance, they will still allow a spark to pass, either as a unit from pole to pole, or as one losing itself in branches, each time a small spark is drawn from the negative side of the machine, provided that the outer coatings of the condensers are connected by a conductor; and further that nothing of the kind takes place when the condensers are insulated from each other, nor when the small spark is taken from the positive side of the machine.

It may be well to state that the size of the small spark necessary to cause the discharge between the poles is not the same under all conditions. When the poles are separated but little beyond their sparking distance it may be very slight, but has to be much larger when the distance between the poles is greatly increased.

The experiments of Lodge and others on the importance of electrical surges and oscillations in the production of sparks, would incline one to attribute the above phenomenon to some such cause. There is, however, one important objection to this explanation. If the phenomenon is really due to surges or oscillations, it is not clear why they should not be equally great, and the results just as pronounced when the side spark is taken from one pole as when it is taken from the other. Still, the fact that the phenomenon ceases when and only when the outer coatings of the jars are so insulated that there can be no oscillations or even surges between them, well nigh compells the acceptance of the above explanation, but in a distinctly modified form.

Let the jars be fully charged, and the poles separated too far to allow sparks to pass under ordinary conditions. The field of force due to these charges is a complicated one, depending of course to some extent on neighboring objects, but as a rough approximation it may be regarded as made up of lines of force between the poles A and B say of the figure, and a much greater number of lines

of force from inner to outer coatings through the walls of the jars *J, J*. If the jars are insulated from each other a spark drawn from either *A* or *B* will decrease the strain between them. I assume the sparks to be taken with objects in connection with the earth, that is at zero potential. If, on the other hand, the outside coatings of the jars are so connected that oscillations or even one-way surges may pass between them a spark from either pole will cause an impulsive rush of the opposite charge to the other pole and a consequent rise of its potential. That the break-down takes place only when the auxiliary spark is taken from the negative side indicates that the dielectric is far more sensitive to shocks next the anode than it is next the cathode.

There are other indications, at least one of which I shall discuss in another paper, of the superior sensitiveness to electrical disturbances of the region about the positive over that about the negative pole. But this idea of sensitiveness of the dielectric next the anode, when under usual conditions, is already supported by certain experiments of Faraday, Macfarlane and De la Rue and Hugo Müller. In speaking of Faraday's experiments on discharges between spheres of different sizes, J. J. Thomson[1] says: "We may express this result by saying that when the electric field is not uniform the gas does not break down so easily when the greatest electromotive intensity is at the cathode as it does when it is at the anode."

To explain this sensitiveness at the anode, we may assume that the molecules of the dielectric between the poles are polarized and formed into Grotthus' chains, and further that these chains are more easily broken down or ionized by shocks at one end than by shocks at the other or by steady strains. This hypothesis offers a common explanation of the above phenomenon and Jaumann's discovery[2] that a gas is electrically weaker under oscillating fields than under steady ones.

In the various experiments of Jaumann and other workers on the effects of oscillations in producing sparks there are no indications, so far as I know, whether it is the positive to negative pole or the reverse impulse that produces the spark, but if the above

[1] Experimental Researches, p. 170.

[2] Sitzb. d. Wien Akad., 97, p. 765, 1888.

assumptions are true it would seem to be the former and not the latter.

Doubtless more or less close mechanical analogies to the assumption of a Grotthus' chain more sensitive to shocks at one end than at the other could be found, but at present I shall not search for them, since the assumption is offered more as a means of coördinating this with other experiments, and of suggesting possible lines of further work than as a complete and final explanation.

ROUSS PHYSICAL LABORATORY,
UNIVERSITY OF VA., March, 1900.

INDEX TO VOLUME X.

A.

Acetylene flame, temperature of the, *Nichols*, 234.

Acoustic analyses of vowels from the phonographic record, *Bevier*, 193.

Adams, C. F., An apparatus for determining the coefficient of expansion of air at constant pressure, 178.

Aimé, G., *De l'influence de la pression sur les actions chemiques*, 190.

Air at constant pressure, apparatus for determining the coefficient of expansion of, *Adams*, 178.

Ångström, K., An objective representation of the hysteresis of iron and steel, 74.

Anodes, size of as influencing deposit of silver voltameters, *Merrill*, 167.

Arc, a dissociation theory of the electric, *Child*, 151.

B.

Baker, W. C., A lecture demonstration in wave motion, 175.

Barnes, H. T., An hermetically sealed type of Clark standard cell, 268.

Variation of specific heat of water between 0° and 100° C.

Barnett, S. J., The influence of electrification on the surface tension of water and mercury, 65.

Barus, Carl, Scheiner's *Strahlung und Temperatur der Sonne*, 126.

Transmission of the ionized exhalations of phosphorus through air and other media, 257.

Benzene, revision of some thermal data concerning, *Tsuruta*, 116.

Bevier, L., Jr., Acoustic analysis of vowels from the phonographic record, 193.

Book reviews.

American telephone practice, *Miller*, 192.

Elements of alternating currents, *Franklin and Williamson*, 189.

Elements of physics, *Crew*, 254.

Geschichte der physikalischen experimentierkunst, *Gerland und Traumüller*, 127.

Influence de la pression sur les actions chemiques, *Aimé*, 190.

Lehrbuch der experimental Physik, *Wüllner*, 63.

Ostwald's Klassiker der exakten Wissenschaften, Nos. 99 and 100, 63.

Strahlung und Temperatur der Sonne, *Scheiner*, 126.

Text-book of physics, *Watson*, 255.

Text-book of physics, *Wentworth and Hill*, 187.

Traité élémentaire de mechanique chemique fondeé sur la Thermodynamique, *Duhem*, 191.

Boyle's law apparatus, an efficient, *Humphreys*, 123.

Boynton, Gibbs' thermodynamic model, 228.

Cajori, F., Gerland and Traumüller's Geschichte der Physikalischen Experimentierkunst, 127.

Callender, H. L., Variation of specific heat of water between 0° and 100° C., 202.

Carpenter, H. V., A new method of comparing two self-inductances, 52.

Cell, an hermetically sealed type of Clark standard, Barnes, 268.

Child, C. D., A dissociation theory of the electric arc, 151.

Copper voltameter, polarization and internal resistance of, *Moore*, 34.

Crew, H., *Elements of Physics*, 254.

D.

Density and elasticity of the ether, *Fessenden*, 1, 83.

Dissociation theory of the electric arc, *Child*, 151.
Duhem, P., *Traitè élèmentaire de mechanique chemique fondeè sur la Thermodynamique*, *Duhem*, 191.

E.

Elasticity and density of the ether, *Fessenden*, 1, 83.
Elasticity of rods, effect of magnetization on, *Stevens*, 161.
Electric and magnetic quantities, determination of nature of, *Fessenden*, 1, 83.
Electrification, influence of on the surface tension of water and mercury, *Merritt and Barnett*, 65.
Ether, elasticity and density of the, *Fessenden*, 1, 83.
Expansion of air at constant pressure, apparatus for determining the coefficient of, *Adams*, 178.

F.

Fessenden, R. A., A determination of the nature of the electric and magnetic quantities, and of the density and elasticity of the ether, 1, 83.
Franklin, W. S., Aimé's *De l'influence de la pression sur les action chemiques*, 190.
Duhem's Traité élémentaire de Mechanique chemique fondeé sur la Thermodynamique, 191.
Elements of Alternating Currents, 189.

G.

Gerland, E., *Geschichte der Physikalischen Experimentierkunst*, 127.

H.

Hall, E. H., Concerning thermal conductivity of iron, 277.
Hill, G. A., *Text-book of Physics*, 187.
Hodges, N. D. C., Law of distribution of velocities among gas molecules, 253.
Humphreys, W. J., An efficient Boyle's-law apparatus, 123.
Spark-length of an electric influence machine as modified by a small spark from the negative side, 301.
Hysteresis of iron and steel, an objective representation of, *Ångström*, 74.

I.

Inductance, self, a new method of comparing, *Carpenter*, 52.
Internal resistance and polarization of the copper voltameter, *Moore*, 34.
Iron and steel, an objective representation of the hysteresis of, *Angström*, 74.
Iron, concerning thermal conductivity of, *Hall*, 276.
Iron group, magnetic molecular susceptibility of salts of the iron group, *Liebknecht and Wills*, 215.
Iron, soft, on the change in length in an alternating magnetic field, *Austin*, 180.

K.

Kimball, A. L., Crew's *Elements of Physics*, 254.

L.

Liebknecht, O., magnetic molecular susceptibility of salts of the iron group, 215.
Living body, metabolism of matter in, *Rosa*, 129.

M.

Magnetic and electric quantities, determination of nature of, *Fessenden*, 1, 83.
Magnetic field, on the change in length of soft iron in, *Austin*, 180.
Magnetic molecular susceptibility of salts of the iron group. *Liebknecht and Wills*, 215.
Magnetization, effect of, on the elasticity of rods, *Stevens*, 161.
Mercury and water, influence of electrification on the surface tension of, *Merritt and Barnett*, 65.
Merrill, J. F., The influence of temperature, pressure, used solutions, and sizes of anodes on the deposit of, 167.

Merritt, Ernest, The influence of electrification on the surface tension of water and mercury, 65.
Metabolism of matter in the living body, *Rosa*, 129.
Miller, K. B., *American Telephone Practice*, 192.
Moore, B. E., Polarization and internal resistance of the copper voltameter, 34.

N.

Nichols, E. L., Miller's *American Telephone Practice*, 192.
On the temperature of the acetylene flame, 234.
Ostwald's *Klassiker der Exakten Wissenschaften*, 63.
Watson's *Text-book of Physics*, 255.
Wüllner's *Lehrbuch der experimental Physik*, 63.

P.

Phosphorus, transmission of ionized exhalations of, through air and other media, *Barus*, 257.
Polarization and internal resistance of the copper voltameter, *Moore*, 34.
Pressure, influence of on the deposit of silver voltameters, *Merrill*, 167.

R.

Rosa, E. B., On the metabolism of matter in the living body, 129.

S.

Scheiner, *Strahlung und Temperatur de Sonne*, 126.
Self-inductances, a new method of comparing two, *Carpenter*, 52.
Silver voltameters, the influence of temperature, pressure, used solutions, and size of anodes on the deposit of, *Merrill*, 167.
Smith, H. B., Franklin and Williamson's *Elements of Alternating Currents*, 189.
Solutions, used, influence of on the deposit of silver voltameters, *Merrill*, 167.
Spark-length of an electric influence machine as modified by a small spark from the negative side, *Humphreys*, 301.
Specific heat of water between 0° and 100°C., the variation of, *Callender and Barnes*, 202.
Standard cell, Clark, on hermetically sealed type of, *Barnes*, 268.
Steel and iron, an objective representation of the hysteresis of, *Ångström*, 74.
Stevens, J. S., Effect of magnetism on the elasticity of rods, 161.
Surface tension of water and mercury, influence of electrification on, *Merritt and Barnett*, 65.

T.

Temperature, influence of, on the deposit of silver voltameters, *Merrill*, 167.
Temperature of the acetylene flame, *Nichols*, 234.
Thermal conductivity in iron, *Hall*, 277.
Thermal data concerning benzene, revision of, *Tsuruta*, 116.
Thermodynamic model, Gibbs', *Boynton*, 228.
Thompson, J. O., Wentworth and Hill's *Text-book of Physics*, 187.
Traumüller, F., *Geschichte der Physikalischen Experimentierkunst*, 127.
Tsuruta, K., Thermodynamic notes (No. 10); Revision of some thermal data concerning benzene, 116.

V.

Velocities, law of distribution of, among gas molecules, *Hodges*, 253.
Voltameter, copper, polarization and internal resistance of, *Moore*, 34.
Voltameters, silver, the influence of temperature, pressure, used solutions, and size of anodes on the deposit of, *Merrill*, 167.
Vowels, acoustic analysis of, from the phonographic record, *Bevier*, 193.

W.

Water and mercury, influence of electrification on surface tension of, *Merrill and Barnett*, 65.

Water, variation of specific heat of, between 0° and 100° C., *Callender and Barnes*, 202.

Wave motion, a lecture demonstration of, Baker, 175.

Watson, W., *Text-book of Physics*, 255.

Wentworth, G. A., *Text-book of Physics*, 187.

Williamson, R. B., *Elements of Alternating Currents*, 189.

Wills, A. P., Magnetic molecular susceptibility of salts of the iron group, 215.

Wüllner, A., *Lehrbuch der Experimental Physik*, 63.